

PATENT APPLICATION

Xerox Docket No. D/A3533

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE HONORABLE BOARD OF PATENT APPEALS AND INTERFERENCES

In re the Application of

Judith M. VANDEWINCKEL et al.

Application No.: 10/743,097

Examiner: C. RODEE

Filed: December 23, 2003

Docket No.: 117545

For: EMULSION AGGREGATION TONER HAVING RHEOLOGICAL AND FLOW
PROPERTIES

BRIEF ON APPEAL

Appeal from Group 1756

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I. REAL PARTY IN INTEREST

The real party in interest for this appeal and the present application is Xerox Corporation, by way of an Assignment recorded in the U.S. Patent and Trademark Office at Reel 014842, Frame 0139.

II. STATEMENT OF RELATED APPEALS AND INTERFERENCES

There are no prior or pending appeals, interferences or judicial proceedings, known to Appellant, Appellant's representative, or the Assignee, that may be related to, or which will directly affect or be directly affected by or have a bearing upon, the Board's decision in the pending appeal.

III. STATUS OF CLAIMS

Claims 1-19 are on appeal.

Claims 1-19 are pending.

Claims 1-19 are rejected.

IV. STATUS OF AMENDMENTS

No Amendment After Final Rejection has been filed. A Request for Reconsideration and Rule 132 Declaration were filed on June 29, 2006. In a July 12, 2006 Advisory Action, the Examiner indicated that the Request for Reconsideration and Rule 132 Declaration were considered, but did not place the application in condition for allowance.

V. SUMMARY OF CLAIMED SUBJECT MATTER

The claimed subject matter is directed to toners and developers containing the toners for use in forming and developing images of good quality and gloss. As explained at page 1, paragraph [0001] of the specification, the novel combination of rheological and powder flow properties of the toner particles achieves advantageous results.

A. Independent Claim 1

Claim 1 is directed to a toner including toner particles comprising a styrene acrylate binder and at least one colorant. See paragraph [0010]. The styrene acrylate binder has a weight average molecular weight of about 20 to about 30 kpe and a molecular peak of about 23 to about 28 kpe. See paragraphs [0030], [0031] and [0032]. The toner particles have a weight average molecular weight of about 28 to about 130 kpe, a number average molecular weight of about 9 to about 13.4 kpe and a MWD of about 2.2 to about 10. See paragraph [0032]. Also, the toner particles have a cohesion of about 55 to about 98% at a mean circularity of about 0.94 to about 0.98. See paragraph [0034].

As explained at paragraph [0034], a significant property of the toners is the cohesivity of the particles prior to inclusion of any external additives. The greater the cohesivity, the less the toner particles are able to flow. It was surprisingly found in the present application that the cohesivity of the toner particles, prior to inclusion of any external additives, should be from about 55 to about 98% for all colors of the toner.

As described in paragraph [0034], cohesivity with respect to flow is measured by placing a known mass of toner, for example two grams, on top of a set of three screens, for example with screen meshes of 53 microns, 45 microns, and 38 microns in order from top to bottom, and vibrating the screens and toner for a fixed time at a fixed vibration amplitude, for example for 115 seconds at a 1 millimeter vibration amplitude. A device to perform this measurement is a Hosokawa Powders Tester, available from Micron Powders Systems. The

toner cohesion value is related to the amount of toner remaining on each of the screens at the end of the time. A cohesion value of 100% corresponds to all of the toner remaining on the top screen at the end of the vibration step and a cohesion value of zero corresponds to all of the toner passing through all three screens, that is, no toner remaining on any of the three screens at the end of the vibration step. The higher the cohesion value, the lesser the flowability of the toner.

B. Independent Claim 18

Claim 18 is directed to a set of toners for forming a color image, comprising a cyan toner, a magenta toner, a yellow toner and a black toner, wherein each of the cyan toner, the magenta toner, the yellow toner and the black toner comprise toner particles comprised of about 70 to about 95% by weight, solids basis, of a styrene acrylate binder, about 5 to about 15% by weight, solids basis, of a wax dispersion, and at least one colorant. See paragraph [0009] and [0017]. As in claim 1 above, the styrene acrylate binder has a weight average molecular weight of about 20 to about 30 kpse and a molecular peak of about 23 to about 28 kpse, and the toner particles have a weight average molecular weight of about 28 to about 130 kpse, a number average molecular weight of about 9 to about 13.4 kpse and a MWD of about 2.2 to about 10, and a cohesion of about 55 to about 98% at a mean circularity of about 0.94 to about 0.98. See paragraphs [0030] to [0034].

VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

The following grounds of rejection are presented for review:

Claims 1-19 are rejected as indefinite under 35 U.S.C. §112, second paragraph as allegedly failing to particularly point out and distinctly claim the subject matter which applicants regard as the invention.

VII. ARGUMENT

A. Claims 1-19 are not indefinite

Claims 1-19 were rejected under 35 U.S.C. §112, second paragraph as allegedly being indefinite. Applicants respectfully disagree. Applicants submit that the scope of the claims is quite definite in the context of the specification and in view of the knowledge of practitioners in the art.

1. The Claimed "Cohesion" is Definite

The Examiner alleged that the specification does not describe the manner of determining the cohesion value with sufficient particularity so that the artisan would be reasonably apprised of the claimed "cohesion" value.

The present application clearly discloses the method of measuring the cohesion value recited in claim 1. Specifically, at paragraph [0034], the specification discloses using a powder tester device with the known amount of toner being 2 grams, the screen sizes being 53 microns, 45 microns and 38 microns in order from top to bottom, and the amount of time being 115 seconds at a 1 millimeter amplitude vibration. Therefore, the method of measuring for the cohesion value is specifically disclosed in the specification.

The Examiner asserts that the specification fails to provide a reasonable manner of determining how much of the toner needs to be retained on any one, all or some combination of screens in order to obtain a cohesion value of about 55% to about 98%.

Applicants submit that the calculation for cohesion as it relates to flow properties from the results of the above-described measurement is well known in the art. The particle flow values (cohesivity) may be calculated with the use of the well known equation expressed as $\% \text{ cohesion} = 50 \cdot A + 30 \cdot B + 10 \cdot C$, where A is the mass of toner remaining on the top screen, B is the mass of toner remaining on the middle screen, and C is the mass of toner remaining on the bottom screen. While the specification does not explicitly state this

calculation, the specification need not state what is well known in the art. All of the evidence supports that one of ordinary skill in the art would understand to use the well known equation with the measurement techniques described in the specification to obtain the recited cohesion value of the present claims.

A Declaration was filed under 37 CFR §1.132 (see Appendix B) outlining the method and calculation of the cohesion value. In particular, it is well known to use the $50 \cdot A + 30 \cdot B + 10 \cdot C$ cohesion equation with a three screen Hosokawa Powder Test method, including with the screen sizes according to the present application. As summarized in the Rule 132 Declaration, the cohesion equation, as known in the art, is used with a variation of screen sizes to calculate the cohesion value. Thus, as stated in the Declaration, U.S. Patents Nos. 6,673,501 and 6,150,062, the Hosokawa Powder Tester Manual and R. Veregin and R. Bartha, Proceedings of IS&T 14th International Congress on Advances in Non-Impact Printing Technologies, page 358-361, 1998, Toronto all consistently describe calculating cohesion by the use of the equation $\text{cohesion} = 50A + 30B + 10C$, where A is the mass of toner remaining on the top screen, B is the mass of the toner remaining on the middle screen, and C is the mass of the toner remaining on the bottom screen (see col. 48, lines 21-44 of the 501 Patent, column 22, lines 53-60 of the 062 Patent, section 3, paragraph 2 of the Declaration and page 358 of the R. Veregin article), regardless of screen size.*

The Examiner has repeatedly questioned the applicability of this known calculation to the present application, for example because different screen sizes from those used in the 501 Patent are described. However, (1) practitioners in the art recognize the use of this equation

* There is certainly a correlation between screen sizes in conducting the test. However, once appropriate sizes are selected, which sizes are described in the present specification, then one understands to apply the known cohesion equation to the results obtained using such set of screens.

with a variation of different screen sizes and (2) the specification provides sufficient information to confirm that the cohesion value is calculated using the well known equation.

First, as known in the art and described in the specification, a cohesion value of 100% corresponds to all of the toner remaining on the top screen at the end of the vibration step, i.e., no flowability. As discussed in the Declaration and in paragraph [0034] of the present specification, the only way to get a 100% value with this result is by use of the 50A equation. For example, when all 2 grams of the toner remain on the top screen, the calculation becomes $\text{cohesion} = 50(2) + 30(0) + 10(0)$, or 100%. The specification thus provides information confirming that a calculation involving 50A must be used to obtain the disclosed 100% cohesion value. That is, the fact that the specification describes the use of 2 gram samples and that all of the sample on the top screen results in 100% cohesion confirms use of a formula involving "50A."

Such confirms use and applicability of the known cohesion equation, as described in the Declaration and claimed in the present application. In other words, from this description, one of ordinary skill in the art would understand "50 x A" was used to get the 100% cohesion value when all toner remains on the top screen, and thus that the conventional $50A + 30B + 10C$ cohesion equation was clearly being used. Therefore, the specification indicates that the cohesion value of the present application is calculated using the well known cohesion equation.

Further, as discussed in the Declaration, practitioners in the art recognize the use of this equation with a variation of different screen sizes. For example, U.S. Patent No. 6,150,062 describes the use of sieves of 45 μm mesh size, 38 μm mesh size, and 26 μm mesh size in which 2 grams of a toner is loaded onto the top 45 μm sieve and a 1 mm vibration is given for 90 seconds, after which the toner of each sieve is weighted and each weight is multiplied by 0.5, 0.3 and 0.1 in order of heaviness, and the values obtained are then

multiplied by 100 (see col. 22, lines 53-60). This is the same as the $50A + 30B + 10C$ calculation. Therefore, the use of this equation with variations of the screen sizes and processing conditions, relative to toner being evaluated, are well recognized in the art.

The Examiner cites U.S. Patent No. 5,519,316 (hereinafter Hagiwara) as allegedly showing that screen sizes different than the screen sizes described in the declaration can be used and that % cohesion is not always calculated by the formula discussed in the declaration.

As described in the Declaration, it is known in the art to use different screen sizes, for example, screen sizes different than the screen sizes described in the present application. Hagiwara describes use of screens of mesh sizes of 150 μm , 75 μm and 45 μm (see column 3, lines 13-16).

Further, Hagiwara describes calculating a cohesion degree by summing up (a), (b) and (c) (see column 3, lines 22-37 of Hagiwara). Although Hagiwara describes calculating a cohesion degree, it is clear from Hagiwara that this is not a cohesion value as related to flow properties as known to one of ordinary skill in the art as in the present application. Hagiwara merely calculates an overall percentage of the retains remaining on the three screens, and does not evaluate the true cohesion of the particles as indicative of the flowability value of the material. Hagiwara uses a standard sum equation that sums up the amount of powder remaining on the screens and multiplies by 100 to obtain a standard percentage of the amount retained. The equation in Hagiwara appears to be a calculation that is used to perform a materials to materials comparison and provides a standard sum equation (for example, in weight % if multiplied by 100, and in ppm if multiplied by 10^6) and does not correlate to the flowability of the particles. Thus, Hagiwara uses a different calculation method that is for a different parameter. The total weight % on the screens is not useful for determining the flowability of the particles. Nowhere does Hagiwara describe cohesion as correlated to the flowability of the particles as in the present application and claims.

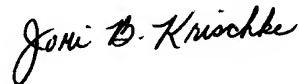
The present specification clearly shows toner flowability measured by the well known cohesion equation. As such, one of ordinary skill in the art would not use the standard sum equation of Hagiwara to calculate a percent cohesion that correlates to the flowability of the particles as in the present application. Instead, as stated above, practitioners in the art would use the well known $50A + 30B + 10C$ equation to calculate % cohesion, particularly in view of the description in the specification as to how to achieve 100% cohesion as discussed above. Hagiwara thus does not provide any evidence refuting the use of the well known cohesion equation in calculating cohesion values as recited in the present claims.

For the foregoing reasons, Applicants submit that the claims are definite. The specification and Declaration confirm calculation of cohesion based on the information given in the specification, and thus recitation of cohesion in the claims is clear and definite to practitioners in the art.

VIII. CONCLUSION

For all of the reasons discussed above, it is respectfully submitted that the rejections are in error and that claims 1-19 are in condition for allowance. For all of the above reasons, Appellants respectfully request this Honorable Board to reverse the rejections of claims 1-19.

Respectfully submitted,



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APPENDIX A - CLAIMS APPENDIX

CLAIMS INVOLVED IN THE APPEAL:

1. A toner including toner particles comprising a styrene acrylate binder and at least one colorant, and wherein the styrene acrylate binder has a weight average molecular weight of about 20 to about 30 kpse and a molecular peak of about 23 to about 28 kpse, the toner particles have a weight average molecular weight of about 28 to about 130 kpse, a number average molecular weight of about 9 to about 13.4 kpse and a MWD of about 2.2 to about 10, and the toner particles have a cohesion of about 55 to about 98% at a mean circularity of about 0.94 to about 0.98.
2. The toner according to claim 1, wherein the binder comprises about 75 to about 85% by weight of the toner particles on a solids basis.
3. The toner according to claim 1, wherein the toner particles further comprise a wax dispersion.
4. The toner according to claim 3, wherein the wax dispersion is present in an amount of about 8 to about 11% by weight of the toner particles on a solids basis.
5. The toner according to claim 1, wherein the toner is a cyan toner, and the at least one colorant is present in an amount of about 5 to about 8% by weight of the toner particles on a solids basis.
6. The toner according to claim 1, wherein the toner is a magenta toner, and the at least one colorant is present in an amount of about 7 to about 15% by weight of the toner particles on a solids basis.
7. The toner according to claim 1, wherein the toner is a yellow toner, and the at least one colorant is present in an amount of about 5 to about 8% by weight of the toner particles on a solids basis.

8. The toner according to claim 1, wherein the toner is a black toner, and the at least one colorant is present in an amount of about 5 to about 8% by weight of the toner particles on a solids basis.
9. The toner according to claim 1, wherein the toner particles further comprise polyaluminum chloride in an amount up to about 2% by weight of the toner particles on a solids basis.
10. The toner according to claim 1, wherein the toner particles further comprise a colloidal silica in an amount up to about 10% by weight of the toner particles on a solids basis.
11. The toner according to claim 1, wherein the toner particles have a melt flow index (MFI) of from about 18 to about 37 g/10 min.
12. The toner according to claim 1, wherein the toner particles have a stripping force range at 170°C of from about 7 to about 18 mg/cm².
13. The toner according to claim 1, wherein the toner particles have an elastic modulus of about 89,000 to about 130,000 dyn/cm² at 120°C/10 rad/sec.
14. The toner according to claim 1, wherein the toner particles have a bulk density of from about 0.22 to about 0.34 g/cc.
15. The toner according to claim 1, wherein the toner particles have a compressibility of from about 33 to about 51.
16. The toner according to claim 1, wherein the toner particles further comprise one or more external additives selected from the group consisting of silica, titanium dioxide and zinc stearate.
17. The toner according to claim 1, wherein the toner particles are further mixed with carrier particles.

18. A set of toners for forming a color image, comprising a cyan toner, a magenta toner, a yellow toner and a black toner, wherein each of the cyan toner, the magenta toner, the yellow toner and the black toner comprise toner particles comprised of about 70 to about 95% by weight, solids basis, of a styrene acrylate binder, about 5 to about 15% by weight, solids basis, of a wax dispersion, and at least one colorant, and wherein the styrene acrylate binder has a weight average molecular weight of about 20 to about 30 kpse and a molecular peak of about 23 to about 28 kpse, the toner particles have a weight average molecular weight of about 28 to about 130 kpse, a number average molecular weight of about 9 to about 13.4 kpse and a MWD of about 2.2 to about 10, and the toner particles have a cohesion of about 55 to about 98% at a mean circularity of about 0.94 to about 0.98.

19. The set of toners according to claim 18, wherein the toner particles of the cyan and the yellow toner have a weight average molecular weight of about 24 to about 34 kpse, a number average molecular weight of about 9 to about 11 kpse and a MWD of about 2.5 to about 3.3, and wherein the toner particles of the black toner and the magenta toner have a weight average molecular weight of about 30 to about 130 kpse, a number average molecular weight of about 10 to about 13.4 kpse, and a MWD of about 2.2 to about 10.

APPENDIX B - EVIDENCE APPENDIX

A copy of each of the following items of evidence relied on by the Appellant is attached:

The evidence was entered into the record by the Examiner as indicated in the July 12, 2006

Advisory Action.

1. Rule 132 Declaration
2. U.S. Patent No. 6,673,501
3. U.S. Patent No. 6,150,062
4. Hosokawa Powder Tester Manual
5. R. Veregin and R. Bartha, Proceedings of IS&T 14th International Congress on Advances in Non-Impact Printing Technologies, page 358-361, 1998, Toronto

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Judith M. VANDEWINCKEL et al.

Group Art Unit: 1756

Application No.: 10/743,097

Examiner: C. RODBE

Filed: December 23, 2003

Docket No.: 117545

For: EMULSION AGGREGATION TONER HAVING RHEOLOGICAL AND FLOW PROPERTIES

DECLARATION UNDER 37 C.F.R. §1.132

I, Judith M. Vandewinkel, a citizen of the United States, hereby declare and state:

- 1. I am a chemical process engineer and have been employed by Xerox Corporation since 1987. I have had a total of 19 years of work and research experience in toners product delivery and toners manufacture. I have work on 10 different color toner product launches which included platform design, research and development, and product launch and manufacturing implementation. I currently am the lead product development engineer for the first chemical process toner manufactured in two Manufacturing plants in Canada.**
- 2. I am a named inventor in the above-captioned patent application. I am familiar with the application and its prosecution.**
- 3. As known in the art, cohesion can be measured using a powder tester. Specifically, the cohesion value is measured by a common and well known method using a Hosokawa Powder Tester, wherein a known amount of toner is placed on the top screen of a three screen stack and vibration is applied for an amount of time. The cohesivity**

measurements are conducted in order to evaluate the flowability of the toner or the percent cohesion of the particles as a degree of flowability.

After running the test, the cohesion is known to be calculated by the use of the well known equation $50A + 30B + 10C = \text{cohesion}$, wherein A is the mass of toner remaining on the top screen, B is the mass of toner remaining on the middle screen and C is the mass of toner remaining on the bottom screen. The Examiner has already been made aware of several references describing this calculation (see, for example, U.S. Patent Nos. 6,673,501 and 6,150,062, and R. Veregin and R. Bartha, Proceedings of IS&T 14th International Congress on Advances in Non-Impact Printing Technologies, page 358-361, 1998, Toronto).

4. The Examiner questions whether the practitioner would have known to use the formula to calculate the cohesion value with screen sizes of 53 μm , 45 μm and 38 μm . As summarized below, there is more than sufficient evidence supporting that one would have known to use the known formula with the screen sizes and test method described in the present specification.

5. First, the specification explains that if all of the 2 gram sample tested remains on the top screen, the cohesion is 100%. The only way to get 100% cohesion with a 2 gram sample is from $(50) \times (2)$, or 50A. As such, this alone would confirm use of the formula $50A + 30B + 10C$ in determining the cohesion value in the present application.

6. Second, it is known in the art to use different screen sizes, depending on different powder properties, and still use the same formula in determining cohesion. For example, the Hosokawa Powder Manual itself (attached) describes the use of different screens for powders with different densities. See page 12 of the Manual, indicating screen sizes of 200 mesh, 100 mesh and 60 mesh for powders of 0.4-0.9 gm/cc bulk density, and page 15 of the Manual, indicating screen sizes of 42, 60 and 100 mesh for lighter powders and screen sizes of 100, 200 and 350 mesh for heavier powders. However, all use the same cohesion

equation in calculating cohesion. Different sizes of powders also necessitate different screen sizes. For example, U.S. Patent No. 6,150,062 uses screen sizes of 45 μ m, 38 μ m and 26 μ m, different from the Manual, but still determining cohesion using the cohesion formula. Also, U.S. Patent No. 6,673,501, referencing R. Veregin and R. Bartha, Proceedings of IS&T 14th International Congress on Advances in Non-Impact Printing Technologies, uses screen sizes of 150, 75 and 45 microns. In the present case, because the powders are < 12 μ m, appropriate screen sizes were selected to be 53 μ m, 45 μ m and 38 μ m, as similarly described in U.S. Patents Nos. 6,083,654, 6,850,725 and 6,824,924. Thus, it is known to select different screen sizes for the three screens, depending on different properties of the powders tested, and still use the same cohesion equation.

7. Third, it is known in the art generally that the three screen Hosokawa Powder Test (regardless of screen sizes) gives results from which cohesion is always calculated via $50A + 30B + 10C$. In other words, mention of the use of a Hosokawa Powder Tester alone tells one of ordinary skill in the art that cohesion is calculated from the known cohesion equation. The Examiner has provided no evidence of any other formulas that may be used for the calculation of cohesion when using the Hosokawa Powder Tester. One informed of the use of the Hosokawa Powder Tester, the three screen sizes to use and the vibration amplitude will be fully informed as to how to run the test and also how to calculate cohesion (using $50A + 30B + 10C$), as such is the only standard cohesion calculation from a Hosokawa Powder Test.

8. As evident from the above, the use of the cohesion equation $50A + 30B + 10C$ is known for various screen sizes and processing conditions dependent upon the powders evaluated. In the present application, more than sufficient disclosure is given to confirm the use of such an equation with the results obtained from the Hosokawa Powder Tester. The cohesion value as recited in the claims is quite clear to a practitioner in the art.

9. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date:

6-28-06

John M. Vandewinkel
John M. Vandewinkel



US006673501B1

(12) **United States Patent**
Combes et al.(10) **Patent No.: US 6,673,501 B1**
(45) **Date of Patent: *Jan. 6, 2004**(54) **TONER COMPOSITIONS COMPRISING
POLYESTER RESIN AND POLYPYRROLE**(75) **Inventors:** James R. Combes, Burlington (CA);
Karen A. Moffat, Brantford (CA);
Maria N. V. McDougall, Burlington
(CA)(73) **Assignee:** Xerox Corporation, Stamford, CT
(US)(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 61 days.This patent is subject to a terminal dis-
claimer.(21) **Appl. No.: 09/723,911**(22) **Filed: Nov. 28, 2000**(51) **Int. Cl.⁷ G03G 9/097**(52) **U.S. Cl. 430/108.22; 430/109.4;**
430/110.2; 430/137.11; 430/137.14(58) **Field of Search 430/108.22, 110.2,**
430/137.14, 137.12, 137.2, 137.19, 110,
109.4, 137.11(56) **References Cited****U.S. PATENT DOCUMENTS**

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* cited by examiner

Primary Examiner—Janis L. Dote(74) *Attorney, Agent, or Firm*—Judith L. Byorick(57) **ABSTRACT**

Disclosed is a toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process. Another embodiment of the present invention is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process.

38 Claims, 12 Drawing Sheets

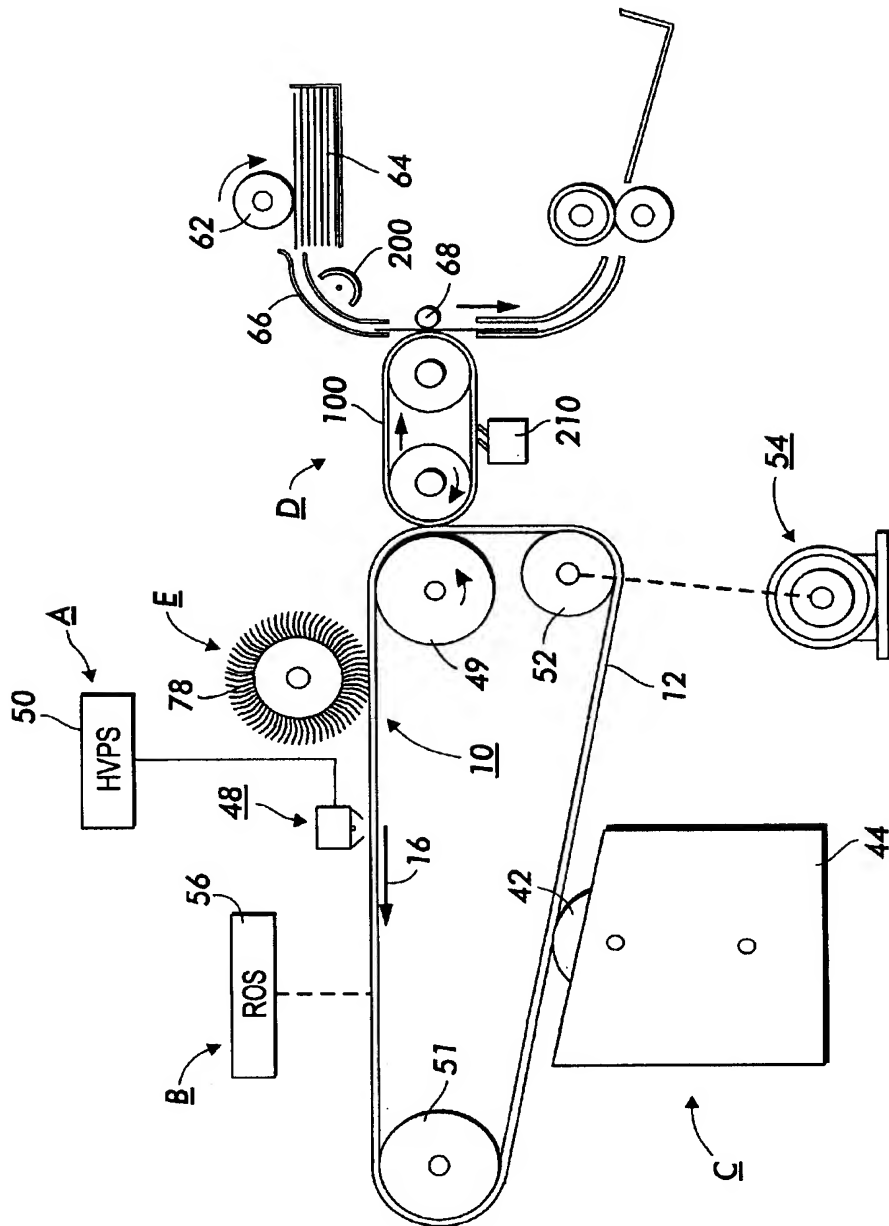


FIG. 1

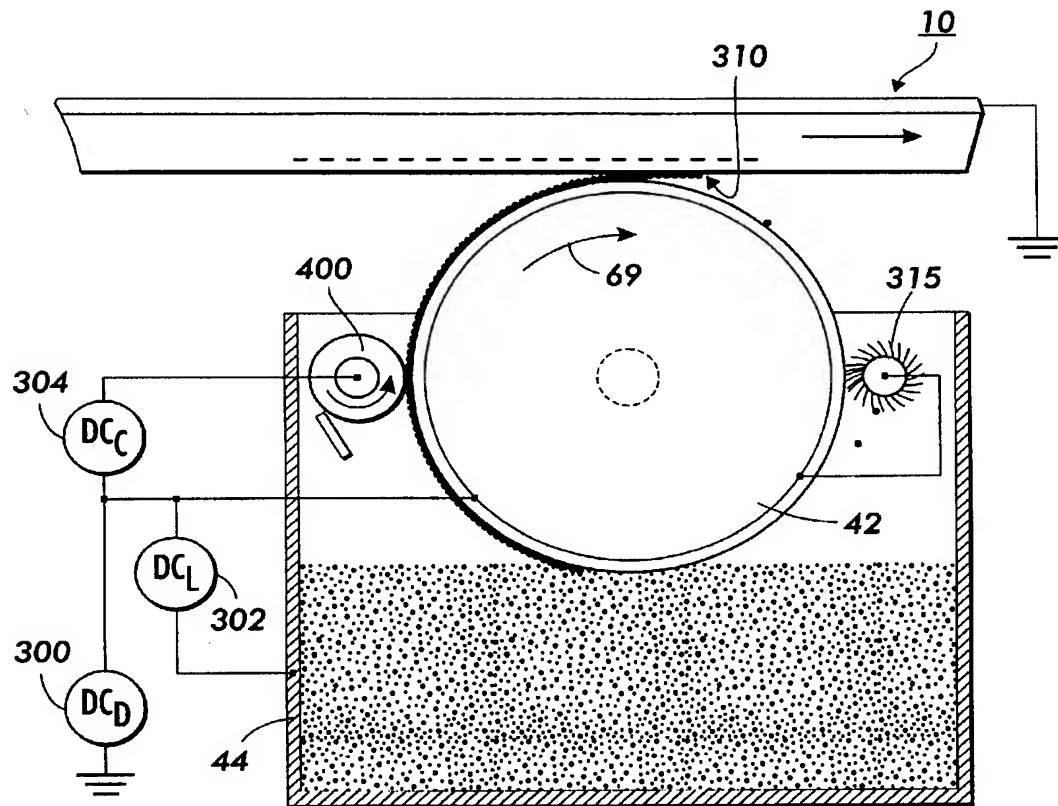
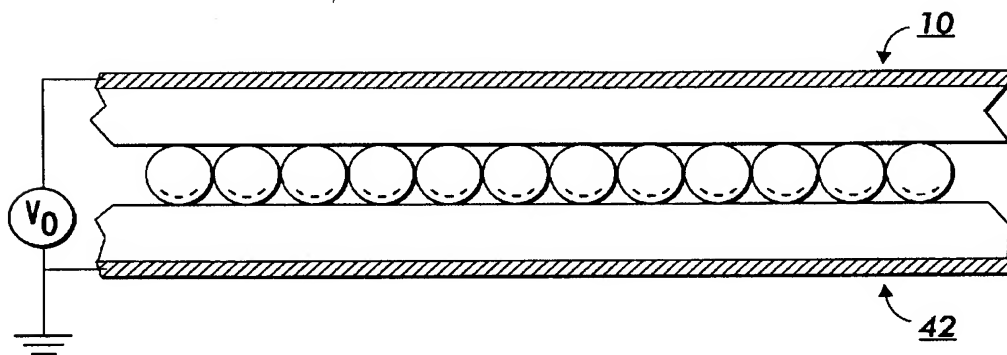
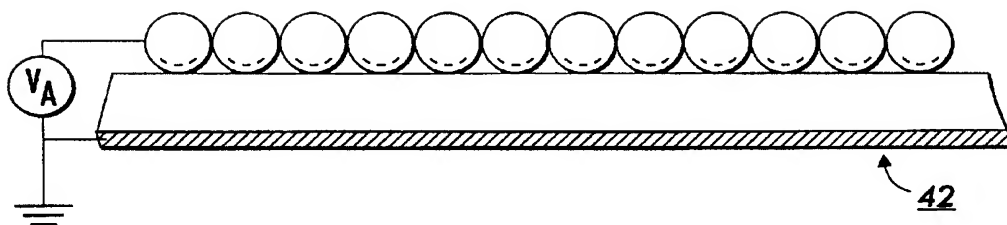


FIG. 2

FIG. 3**FIG. 4**

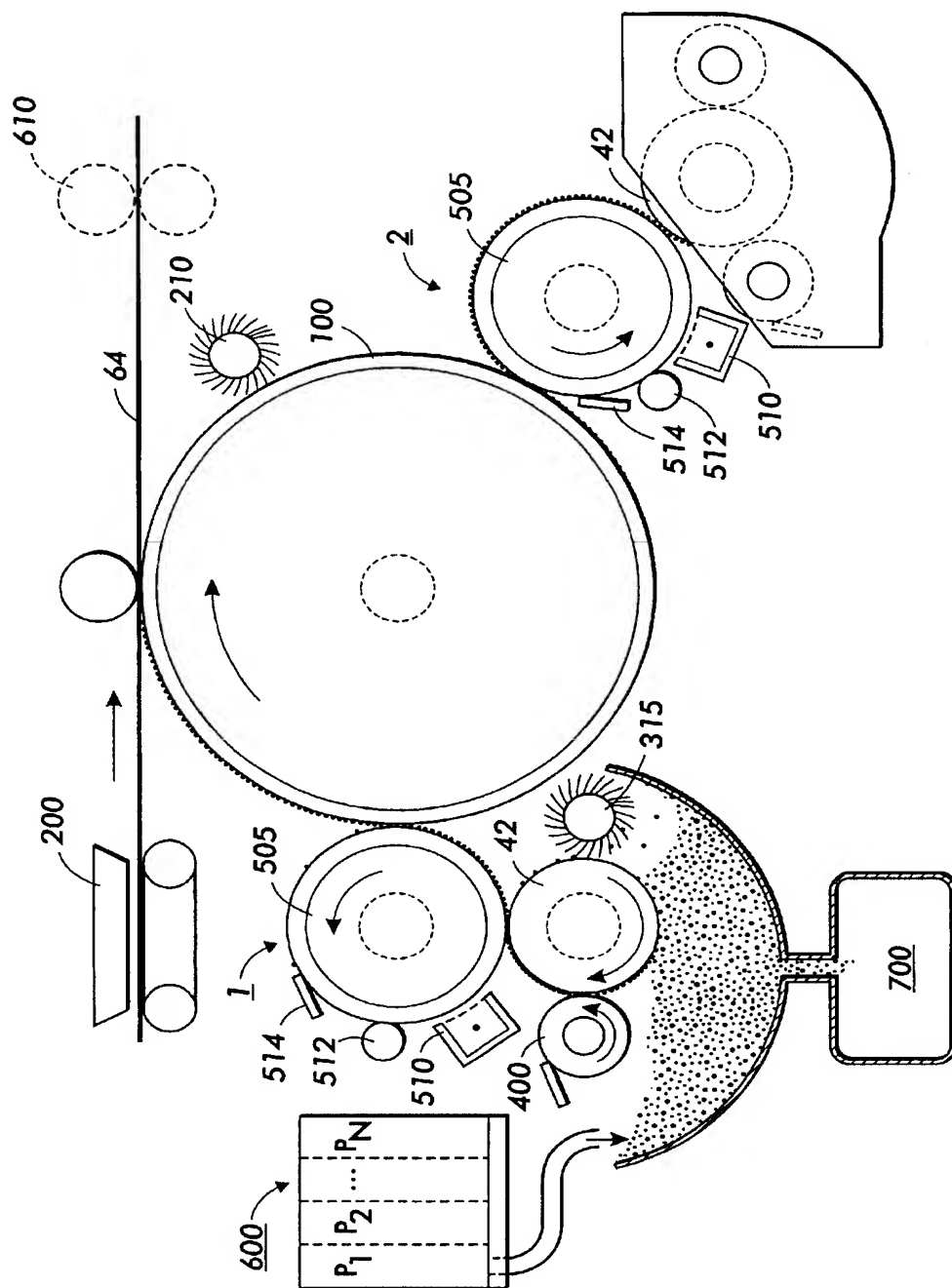
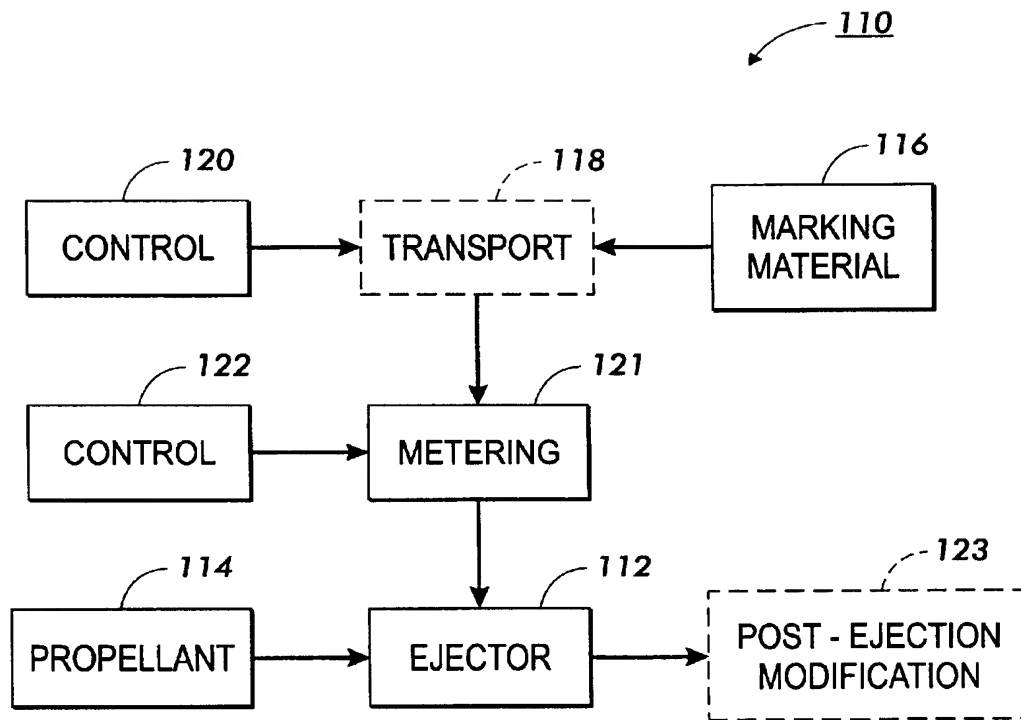


FIG. 5

**FIG. 6**

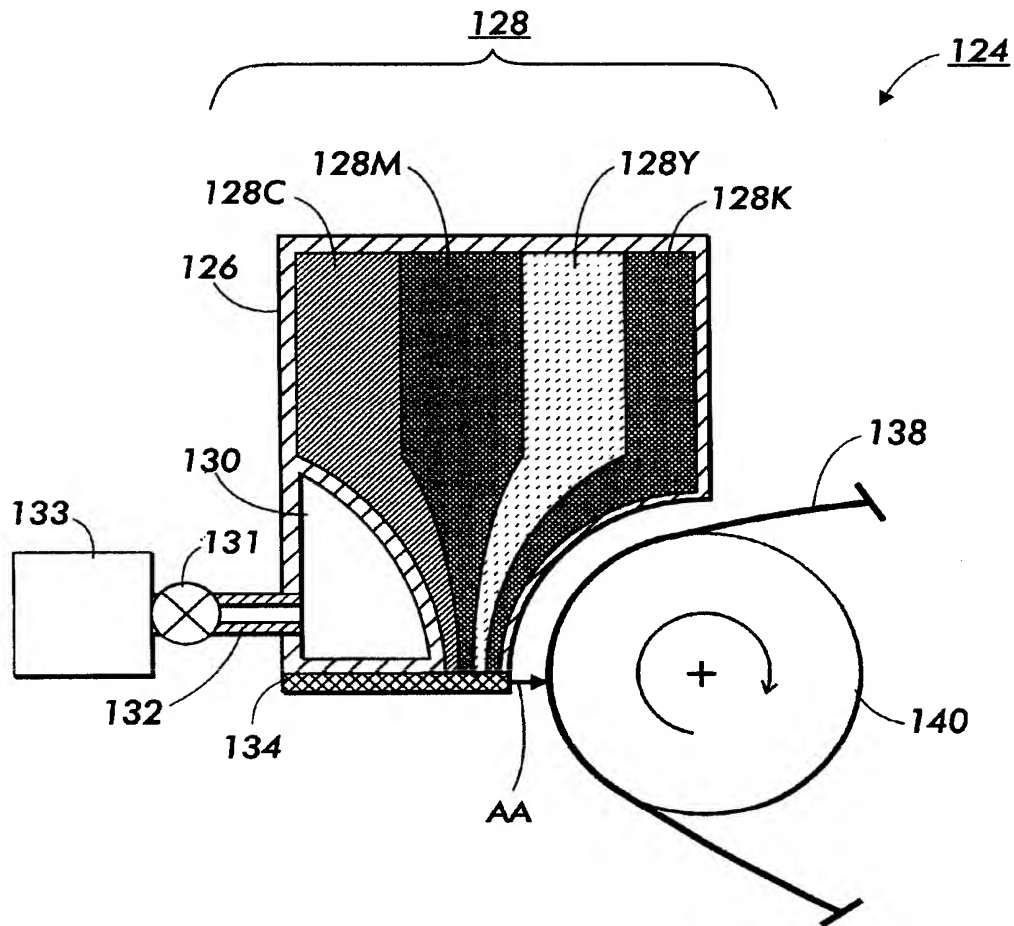


FIG. 7

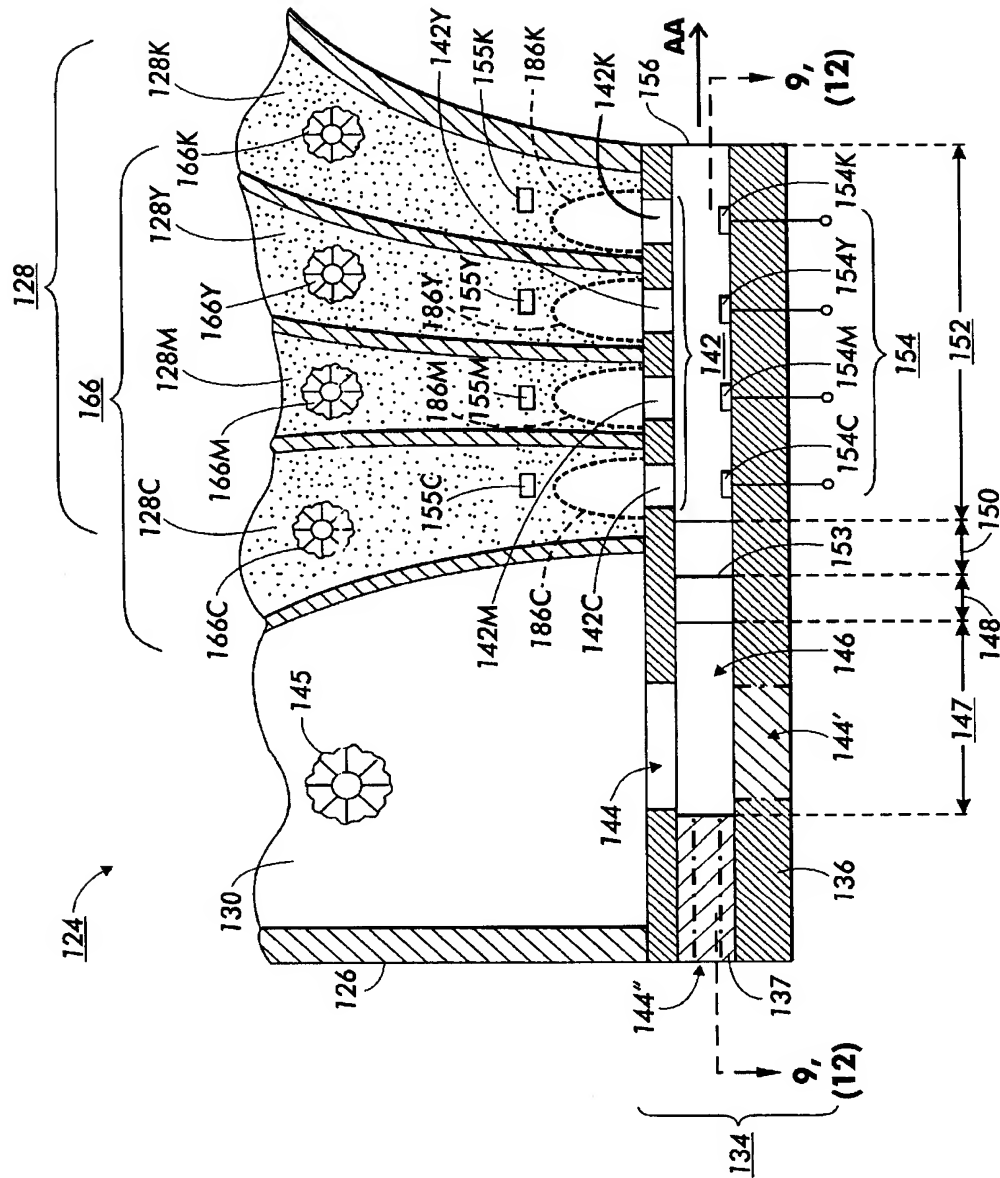


FIG. 8

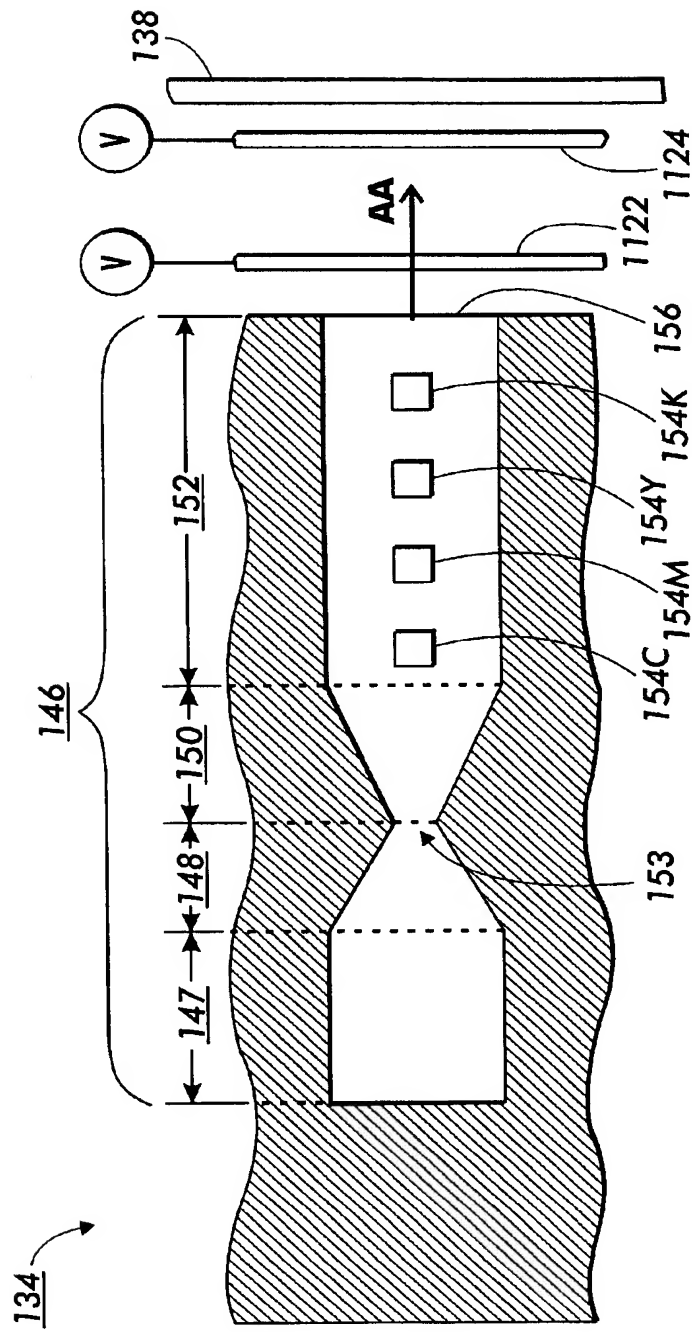


FIG. 9

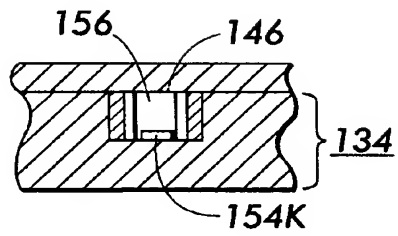


FIG. 10A

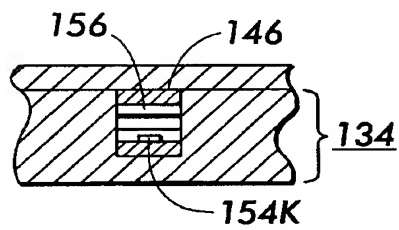


FIG. 10B

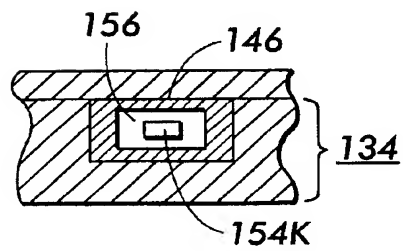


FIG. 10C

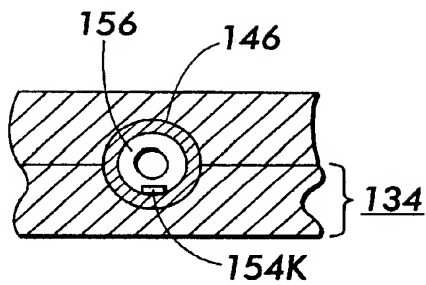


FIG. 11A

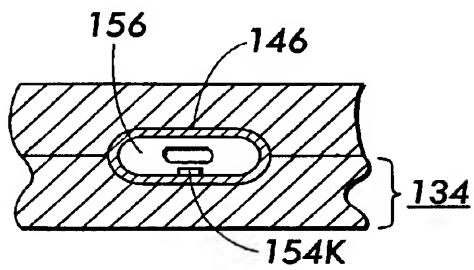


FIG. 11B

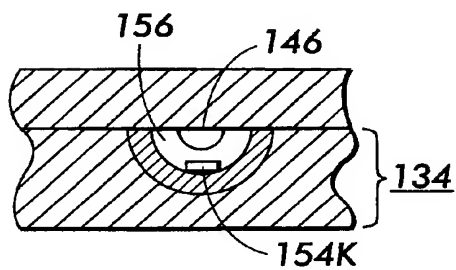


FIG. 11C

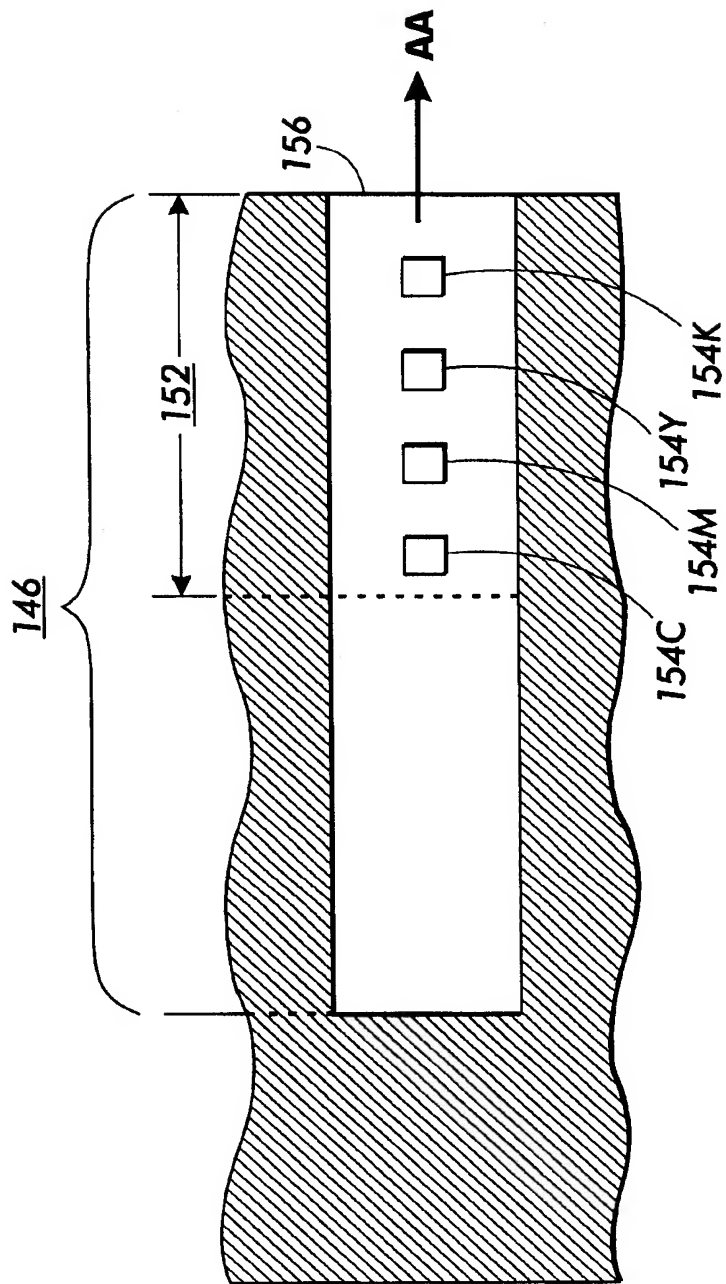


FIG. 12

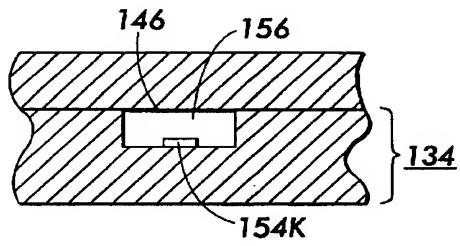


FIG. 13A

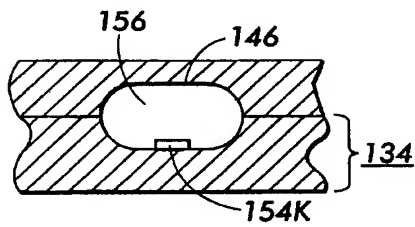


FIG. 13B

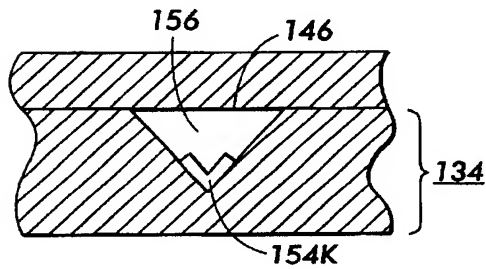


FIG. 13C

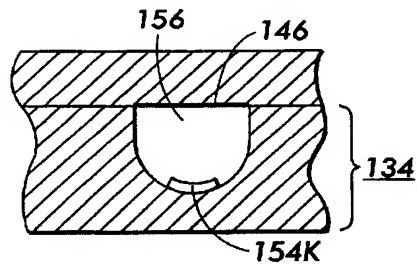


FIG. 13D

TONER COMPOSITIONS COMPRISING POLYESTER RESIN AND POLYPYRROLE

CROSS REFERENCES TO RELATED APPLICATIONS

Application U.S. Ser. No. 09/408,606, now U.S. Pat. No. 6,137,387, filed Sep. 30, 1999, entitled "Marking Materials and Marking Processes Therewith," with the named inventors Richard P. Veregin, Carl P. Tripp, Maria N. McDougall, and T. Brian McAnaney, the disclosure of which is totally incorporated herein by reference, discloses an apparatus for depositing a particulate marking material onto a substrate, comprising (a) a printhead having defined therein at least one channel, each channel having an inner surface and an exit orifice with a width no larger than about 250 microns, the inner surface of each channel having thereon a hydrophobic coating material; (b) a propellant source connected to each channel such that propellant provided by the propellant source can flow through each channel to form propellant streams therein, said propellant streams having kinetic energy, each channel directing the propellant stream through the exit orifice toward the substrate; and (c) a marking material reservoir having an inner surface, said inner surface having thereon the hydrophobic coating material, said reservoir containing particles of a particulate marking material, said reservoir being communicatively connected to each channel such that the particulate marking material from the reservoir can be controllably introduced into the propellant stream in each channel so that the kinetic energy of the propellant stream can cause the particulate marking material to impact the substrate, wherein either (i) the marking material particles of particulate marking material have an outer coating of the hydrophobic coating material; or (ii) the marking material particles have additive particles on the surface thereof, said additive particles having an outer coating of the hydrophobic coating material; or (iii) both the marking material particles and the additive particles have an outer coating of the hydrophobic coating material.

Application U.S. Ser. No. 09/410,271, now U.S. Pat. No. 6,302,513, filed Sep. 30, 1999, entitled "Marking Materials and Marking Processes Therewith," with the named inventors Karen A. Moffat, Richard P. Veregin, Maria N. McDougall, Philip D. Floyd, Jaan Noolandi, T. Brian McAnaney, and Daniele C. Boils, the disclosure of which is totally incorporated herein by reference, discloses a process for depositing marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having a channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel directing the propellant stream toward the substrate, and (b) controllably introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises particles which comprise a resin and a colorant, said particles having an average particle diameter of no more than about 7 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said particles are prepared by an emulsion aggregation process.

Application U.S. Ser. No. 09/585,044, retiled as 09/863,032, which is now U.S. Pat. No. 6,137,387, filed Jun. 1, 2000, entitled "Marking Material and Ballistic Aerosol

Marking Process for the Use Thereof," with the named inventors Maria N. V. McDougall, Richard P. N. Veregin, and Karen A. Moffat, the disclosure of which is totally incorporated herein by reference, discloses a marking material comprising (a) toner particles which comprise a resin and a colorant, said particles having an average particle diameter of no more than about 7 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, and (b) hydrophobic conductive metal oxide particles situated on the toner particles. Also disclosed is a process for depositing marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having a channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel directing the propellant stream toward the substrate, and (b) controllably introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises (a) toner particles which comprise a resin and a colorant, said particles having an average particle diameter of no more than about 7 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, and (b) hydrophobic conductive metal oxide particles situated on the toner particles.

Application U.S. Ser. No. 09/723,778, now U.S. Pat. No. 6,383,561 B1, filed concurrently herewith, entitled "Ballistic Aerosol Marking Process Employing Marking Material Comprising Vinyl Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Karen A. Moffat and Maria N. V. McDougall, the disclosure of which is totally incorporated herein by reference, discloses a process for depositing marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having at least one channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel directing the propellant stream toward the substrate, and (b) controllably introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises toner particles which comprise a vinyl resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), said toner particles having an average particle diameter of no more than about 10 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, said toner particles having an average bulk conductivity of at least about 10^{-11} Siemens per centimeter.

Application U.S. Ser. No. 09/723,577 now U.S. Pat. No. 6,467,871 B1, filed concurrently herewith, entitled "Ballistic Aerosol Marking Process Employing Marking Material Comprising Vinyl Resin and Poly(3,4-ethylenedioxypyrrole)," with the named inventors Karen A. Moffat, Rina Carlini, Maria N. V. McDougall, and Paul J. Gerroir, the disclosure of which is totally incorporated herein by reference, discloses a process for depositing

marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having at least one channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel directing the propellant stream toward the substrate, and (b) controllably introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises toner particles which comprise a vinyl resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), said toner particles having an average particle diameter of no more than about 10 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, said toner particles having an average bulk conductivity of at least about 10^{-11} Siemens per centimeter.

Application U.S. Ser. No. 09/724,458, now U.S. Pat. No. 6,503,678 B1, filed concurrently herewith, entitled "Toner Compositions Comprising Polythiophenes," with the named inventors Karen A. Moffat, Maria N. V. McDougall, Rina Carlini, Dan A. Hays, Jack T. LeStrange, and Paul J. Gerroir, the disclosure of which is totally incorporated herein by reference, discloses a toner comprising particles of a resin and an optional colorant, said toner particles having coated thereon a polythiophene. Another embodiment is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a resin and an optional colorant, said toner particles having coated thereon a polythiophene.

Application U.S. Ser. No. 09/723,839 now U.S. Pat. No. 6,492,082 B1, filed concurrently herewith, entitled "Toner Compositions Comprising Polypyrroles," with the named inventors Karen A. Moffat, Maria N. V. McDougall, Rina Carlini, Dan A. Hays, Jack T. LeStrange, and James R. Combes, the disclosure of which is totally incorporated herein by reference, discloses a toner comprising particles of a resin and an optional colorant, said toner particles having coated thereon a polypyrrole. Another embodiment is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a resin and an optional colorant, said toner particles having coated thereon a polypyrrole.

Application U.S. Ser. No. 09/723,787, now U.S. Pat. No. 6,439,711 B1, filed concurrently herewith, entitled "Ballistic Aerosol Marking Process Employing Marking Material Comprising Polyester Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Rina Carlini, Karen A. Moffat, Maria N. V. McDougall, and Danielle C. Boils, the disclosure of which is totally incorporated herein by reference, discloses a process for depositing marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having at least one channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel directing the propellant stream toward the substrate, and (b) controllably

introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises toner particles which comprise a polyester resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), said toner particles having an average particle diameter of no more than about 10 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, said toner particles having an average bulk conductivity of at least about 10^{-11} Siemens per centimeter.

Application U.S. Ser. No. 09/723,834, now U.S. Pat. No. 6,387,442 B1, filed concurrently herewith, entitled "Ballistic Aerosol Marking Process Employing Marking Material Comprising Polyester Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Karen A. Moffat, Rina Carlini, and Maria N. V. McDougall, the disclosure of which is totally incorporated herein by reference, discloses a process for depositing marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having at least one channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel directing the propellant stream toward the substrate, and (b) controllably introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises toner particles which comprise a polyester resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), said toner particles having an average particle diameter of no more than about 10 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, said toner particles having an average bulk conductivity of at least about 10^{-11} Siemens per centimeter.

Application U.S. Ser. No. 09/724,064, filed concurrently herewith, entitled "Toner Compositions Comprising Polyester Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Karen A. Moffat, Rina Carlini, Maria N. V. McDougall, Dan A. Hays, and Jack T. LeStrange, the disclosure of which is totally incorporated herein by reference, discloses a toner comprising particles of a polyester resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process. Another embodiment is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a polyester resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process.

Application U.S. Ser. No. 09/723,851 now U.S. Pat. No. 6,485,874, B1, filed concurrently herewith, entitled "Toner Compositions Comprising Vinyl Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Karen A. Moffat, Maria N. V. McDougall, Rina Carlini, Dan A. Hays, Jack T. LeStrange, and Paul J. Gerroir, the disclosure of which is totally incorporated herein by reference, discloses a toner comprising particles of a vinyl resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said

toner particles are prepared by an emulsion aggregation process. Another embodiment is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a vinyl resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process.

Application U.S. Ser. No. 09/723,907, now U.S. Pat. No. 6,387,581 B1, filed concurrently herewith, entitled "Toner Compositions Comprising Polyester Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Karen A. Moffat, Rina Carlini, Maria N. V. McDougall, Dan A. Hays, and Jack T. LeStrange, the disclosure of which is totally incorporated herein by reference, discloses a toner comprising particles of a polyester resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process. Another embodiment is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a polyester resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process.

Application U.S. Ser. No. 09/724,013, filed concurrently herewith, entitled "Toner Compositions Comprising Vinyl Resin and Poly(3,4-ethylenedioxythiophene)," with the named inventors Karen A. Moffat, Maria N. V. McDougall, Rina Carlini, Dan A. Hays, Jack T. LeStrange, and Paul J. Gerroir, the disclosure of which is totally incorporated herein by reference, discloses a toner comprising particles of a vinyl resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process. Another embodiment is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a vinyl resin, an optional colorant, and poly(3,4-ethylenedioxythiophene), wherein said toner particles are prepared by an emulsion aggregation process.

Application U.S. Ser. No. 09/723,654, now U.S. Pat. No. 6,365,318 B1, filed concurrently herewith, entitled "Process for Controlling Triboelectric Charging," with the named inventors Karen A. Moffat, Maria N. V. McDougall, and James R. Combes, the disclosure of which is totally incorporated herein by reference, discloses a process which comprises (a) dispersing into a solvent (i) toner particles comprising a resin and an optional colorant, and (ii) monomers selected from pyrroles, thiophenes, or mixtures thereof; and (b) causing, by exposure of the monomers to an oxidant, oxidative polymerization of the monomers onto the toner particles, wherein subsequent to polymerization, the toner particles are capable of being charged to a negative or positive polarity, and wherein the polarity is determined by the oxidant selected.

Application U.S. Ser. No. 09/723,561, now U.S. Pat. No. 6,360,067 B1, filed concurrently herewith, entitled "Electrophotographic Development System With Induction Charged Toner," with the named inventors Dan A. Hays and Jack T. LeStrange, the disclosure of which is totally incorporated herein by reference, discloses an apparatus for developing a latent image recorded on an imaging surface, including a housing defining a reservoir storing a supply of developer material comprising conductive toner; a donor member for transporting toner on an outer surface of said

donor member to a region in synchronous contact with the imaging surface; means for loading a toner layer onto a region of said outer surface of said donor member; means for induction charging said toner loaded on said donor member; means for conditioning toner layer; means for moving said donor member in synchronous contact with imaging member to detach toner from said region of said donor member for developing the latent image; and means for discharging and removing residual toner from said donor and returning said toner to the reservoir.

Application U.S. Ser. No. 09/723,934, now U.S. Pat. No. 6,353,723 B1, filed concurrently herewith, entitled "Electrophotographic Development System With Induction Charged Toner," with the named inventors Dan A. Hays and Jack T. LeStrange, the disclosure of which is totally incorporated herein by reference, discloses a method of developing a latent image recorded or an image receiving member with marking particles, to form a developed image, including the steps of moving the surface of the image receiving member at a predetermined process speed; storing a supply of developer material comprising conductive toner in a reservoir; transporting developer material on a donor member to a development zone adjacent the image receiving member; and; inductive charging said toner layer onto said outer surface of said donor member prior to the development zone to a predefined charge level.

Application U.S. Ser. No. 09/723,789 now U.S. Pat. No. 6,463,239 B1, filed concurrently herewith, entitled "Electrophotographic Development System With Custom Color Printing," with the named inventors Dan A. Hays and Jack T. LeStrange, the disclosure of which is totally incorporated herein by reference, discloses an apparatus for developing a latent image recorded on an imaging surface, including: a first developer unit for developing a portion of said latent image with a toner of custom color, said first developer including a housing defining a reservoir for storing a supply of developer material comprising conductive toner; a dispenser for dispensing toner of a first color and toner of a second color into said housing, said dispenser including means for mixing toner of said first color and toner of said second color together to form toner of said custom color; a donor member for transporting toner of said custom color on an outer surface of said donor member to a development zone; means for loading a toner layer of said custom color onto said outer surface of said donor member, and means for inductive charging said toner layer onto said outer surface of said donor member prior to the development zone to a predefined charge level; and a second developer unit for developing a remaining portion of said latent image with toner being substantially different than said toner of said custom color.

BACKGROUND OF THE INVENTION

The present invention is directed to toners suitable for use in electrostatic imaging processes. More specifically, the present invention is directed to toner compositions that can be used in processes such as electrography, electrophotography, ionography, or the like, including processes wherein the toner particles are triboelectrically charged and processes wherein the toner particles are charged by a nonmagnetic inductive charging process. One embodiment of the present invention is directed to a toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process. Another embodiment of the present invention is directed to a process which comprises (a) generating an electrostatic latent image

on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process.

The formation and development of images on the surface of photoconductive materials by electrostatic means is well known. The basic electrophotographic imaging process, as taught by C. F. Carlson in U.S. Pat. No. 2,297,691, entails placing a uniform electrostatic charge on a photoconductive insulating layer known as a photoconductor or photoreceptor, exposing the photoreceptor to a light and shadow image to dissipate the charge on the areas of the photoreceptor exposed to the light, and developing the resulting electrostatic latent image by depositing on the image a finely divided electroscopic material known as toner. Toner typically comprises a resin and a colorant. The toner will normally be attracted to those areas of the photoreceptor which retain a charge, thereby forming a toner image corresponding to the electrostatic latent image. This developed image may then be transferred to a substrate such as paper. The transferred image may subsequently be permanently affixed to the substrate by heat, pressure, a combination of heat and pressure, or other suitable fixing means such as solvent or overcoating treatment.

Another known process for forming electrostatic images is ionography. In ionographic imaging processes, a latent image is formed on a dielectric image receptor or electrophotoreceptor by ion or electron deposition, as described, for example, in U.S. Pat. No. 3,564,556, U.S. Pat. No. 3,611,419, U.S. Pat. No. 4,240,084, U.S. Pat. No. 4,569,584, U.S. Pat. No. 2,919,171, U.S. Pat. No. 4,524,371, U.S. Pat. No. 4,619,515, U.S. Pat. No. 4,463,363, U.S. Pat. No. 4,254,424, U.S. Pat. No. 4,538,163, U.S. Pat. No. 4,409,604, U.S. Pat. No. 4,408,214, U.S. Pat. No. 4,365,549, U.S. Pat. No. 4,267,556, U.S. Pat. No. 4,160,257, and U.S. Pat. No. 4,155,093, the disclosures of each of which are totally incorporated herein by reference. Generally, the process entails application of charge in an image pattern with an ionographic or electron beam writing head to a dielectric receiver that retains the charged image. The image is subsequently developed with a developer capable of developing charge images.

Many methods are known for applying the electroscopic particles to the electrostatic latent image to be developed. One development method, disclosed in U.S. Pat. No. 2,618,552, the disclosure of which is totally incorporated herein by reference, is known as cascade development. Another technique for developing electrostatic images is the magnetic brush process, disclosed in U.S. Pat. No. 2,874,063. This method entails the carrying of a developer material containing toner and magnetic carrier particles by a magnet. The magnetic field of the magnet causes alignment of the magnetic carriers in a brushlike configuration, and this "magnetic brush" is brought into contact with the electrostatic image bearing surface of the photoreceptor. The toner particles are drawn from the brush to the electrostatic image by electrostatic attraction to the undischarged areas of the photoreceptor, and development of the image results. Other techniques, such as touchdown development, powder cloud development, and jumping development are known to be suitable for developing electrostatic latent images.

Powder development systems normally fall into two classes: two component, in which the developer material comprises magnetic carrier granules having toner particles adhering triboelectrically thereto, and single component, which typically uses toner only. Toner particles are attracted

to the latent image, forming a toner powder image. The operating latitude of a powder xerographic development system is determined to a great degree by the ease with which toner particles are supplied to an electrostatic image. Placing charge on the particles, to enable movement and imagewise development via electric fields, is most often accomplished with triboelectricity.

The electrostatic image in electrophotographic copying/printing systems is typically developed with a nonmagnetic, insulative toner that is charged by the phenomenon of triboelectricity. The triboelectric charging is obtained either by mixing the toner with larger carrier beads in a two component development system or by rubbing the toner between a blade and donor roll in a single component system.

Triboelectricity is often not well understood and is often unpredictable because of a strong materials sensitivity. For example, the materials sensitivity causes difficulties in identifying a triboelectrically compatible set of color toners that can be blended for custom colors. Furthermore, to enable "offset" print quality with powder-based electrophotographic development systems, small toner particles (about 5 micron diameter) are desired. Although the functionality of small, triboelectrically charged toner has been demonstrated, concerns remain regarding the long-term stability and reliability of such systems.

In addition, development systems which use triboelectricity to charge toner, whether they be two component (toner and carrier) or single component (toner only), tend to exhibit nonuniform distribution of charges on the surfaces of the toner particles. This nonuniform charge distribution results in high electrostatic adhesion because of localized high surface charge densities on the particles. Toner adhesion, especially in the development step, can limit performance by hindering toner release. As the toner particle size is reduced to enable higher image quality, the charge Q on a triboelectrically charged particle, and thus the removal force ($F=QE$) acting on the particle due to the development electric field E , will drop roughly in proportion to the particle surface area. On the other hand, the electrostatic adhesion forces for tribo-charged toner, which are dominated by charged regions on the particle at or near its points of contact with a surface, do not decrease as rapidly with decreasing size. This so-called "charge patch" effect makes smaller, triboelectric charged particles much more difficult to develop and control.

To circumvent limitations associated with development systems based on triboelectrically charged toner, a non-tribo toner charging system can be desirable to enable a more stable development system with greater toner materials latitude. Conventional single component development (SCD) systems based on induction charging employ a magnetic loaded toner to suppress background deposition. If with such SCD systems one attempts to suppress background deposition by using an electric field of polarity opposite to that of the image electric field (as practiced with electrophotographic systems that use a triboelectric toner charging development system), toner of opposite polarity to the image toner will be induction charged and deposited in the background regions. To circumvent this problem, the electric field in the background regions is generally set to near zero. To prevent deposition of uncharged toner in the background regions, a magnetic material is included in the toner so that a magnetic force can be applied by the incorporation of magnets inside the development roll. This type of SCD system is frequently employed in printing apparatus that also include a transfuse process, since conductive (black) toner may not be efficiently transferred to

paper with an electrostatic force if the relative humidity is high. Some printing apparatus that use an electron beam to form an electrostatic image on an electrophotoreceptor also use a SCD system with conductive, magnetic (black) toner. For these apparatus, the toner is fixed to the paper with a cold high-pressure system. Unfortunately, the magnetic material in the toner for these printing systems precludes bright colors.

Powder-based toning systems are desirable because they circumvent a need to manage and dispose of liquid vehicles used in several printing technologies including offset, thermal ink jet, liquid ink development, and the like. Although phase change inks do not have the liquid management and disposal issue, the preference that the ink have a sharp viscosity dependence on temperature can compromise the mechanical properties of the ink binder material when compared to heat/pressure fused powder toner images.

To achieve a document appearance comparable to that obtainable with offset printing, thin images are desired. Thin images can be achieved with a monolayer of small (about 5 micron) toner particles. With this toner particle size, images of desirable thinness can best be obtained with monolayer to sub-monolayer toner coverage. For low micro-noise images with sub-monolayer coverage, the toner preferably is in a nearly ordered array on a microscopic scale.

To date, no magnetic material has been formulated that does not have at least some unwanted light absorption. Consequently, a nonmagnetic toner is desirable to achieve the best color gamut in color imaging applications.

For a printing process using an induction toner charging mechanism, the toner should have a certain degree of conductivity. Induction charged conductive toner, however, can be difficult to transfer efficiently to paper by an electrostatic force if the relative humidity is high. Accordingly, it is generally preferred for the toner to be rheologically transferred to the (heated) paper.

A marking process that enables high-speed printing also has considerable value.

Electrically conductive toner particles are also useful in imaging processes such as those described in, for example, U.S. Pat. No. 3,639,245, U.S. Pat. No. 3,563,734, European Patent 0,441,426, French Patent 1,456,993, and United Kingdom Patent 1,406,983, the disclosures of each of which are totally incorporated herein by reference.

Marking materials of the present invention are also suitable for use in ballistic aerosol marking processes. Ink jet is currently a common printing technology. There are a variety of types of ink jet printing, including thermal ink jet printing, piezoelectric ink jet printing, and the like. In ink jet printing processes, liquid ink droplets are ejected from an orifice located at one terminus of a channel. In a thermal ink jet printer, for example, a droplet is ejected by the explosive formation of a vapor bubble within an ink bearing channel. The vapor bubble is formed by means of a heater, in the form of a resistor, located on one surface of the channel.

Several disadvantages can be associated with known ink jet systems. For a 300 spot-per-inch (spi) thermal ink jet system, the exit orifice from which an ink droplet is ejected is typically on the order of about 64 microns in width, with a channel-to-channel spacing (pitch) of typically about 84 microns; for a 600 dpi system, width is typically about 35 microns and pitch is typically about 42 microns. A limit on the size of the exit orifice is imposed by the viscosity of the fluid ink used by these systems. It is possible to lower the viscosity of the ink by diluting it with increasing amounts of liquid (such as water) with an aim to reducing the exit orifice

width. The increased liquid content of the ink, however, results in increased wicking, paper wrinkle, and slower drying time of the ejected ink droplet, which negatively affects resolution, image quality (such as minimum spot size, intercolor mixing, spot shape), and the like. The effect of this orifice width limitation is to limit resolution of thermal ink jet printing, for example to well below 900 spi, because spot size is a function of the width of the exit orifice, and resolution is a function of spot size.

Another disadvantage of known ink jet technologies is the difficulty of producing grayscale printing. It is very difficult for an ink jet system to produce varying size spots on a printed substrate. If one lowers the propulsive force (heat in a thermal ink jet system) so as to eject less ink in an attempt to produce a smaller dot, or likewise increases the propulsive force to eject more ink and thereby to produce a larger dot, the trajectory of the ejected droplet is affected. The altered trajectory in turn renders precise dot placement difficult or impossible, and not only makes monochrome grayscale printing problematic, it makes multiple color grayscale ink jet printing impracticable. In addition, preferred grayscale printing is obtained not by varying the dot size, as is the case for thermal ink jet, but by varying the dot density while keeping a constant dot size.

Still another disadvantage of common ink jet systems is rate of marking obtained. Approximately 80 percent of the time required to print a spot is taken by waiting for the ink jet channel to refill with ink by capillary action. To a certain degree, a more dilute ink flows faster, but raises the problem of wicking, substrate wrinkle, drying time, and the like, discussed above.

One problem common to ejection printing systems is that the channels may become clogged. Systems such as thermal ink jet which employ aqueous ink colorants are often sensitive to this problem, and routinely employ non-printing cycles for channel cleaning during operation. This cleaning is required, since ink typically sits in an ejector waiting to be ejected during operation, and while sitting may begin to dry and lead to clogging.

Ballistic aerosol marking processes overcome many of these disadvantages. Ballistic aerosol marking is a process for applying a marking material to a substrate, directly or indirectly. In particular, the ballistic aerosol marking system includes a propellant which travels through a channel, and a marking material that is controllably (i.e., modifiable in use) introduced, or metered, into the channel such that energy from the propellant propels the marking material to the substrate. The propellant is usually a dry gas that can continuously flow through the channel while the marking apparatus is in an operative configuration (i.e., in a power-on or similar state ready to mark). Examples of suitable propellants include carbon dioxide gas, nitrogen gas, clean dry ambient air, gaseous products of a chemical reaction, or the like; preferably, non-toxic propellants are employed, although in certain embodiments, such as devices enclosed in a special chamber or the like, a broader range of propellants can be tolerated. The system is referred to as "ballistic aerosol marking" in the sense that marking is achieved by in essence launching a non-colloidal, solid or semi-solid particulate, or alternatively a liquid, marking material at a substrate. The shape of the channel can result in a collimated (or focused) flight of the propellant and marking material onto the substrate.

The propellant can be introduced at a propellant port into the channel to form a propellant stream. A marking material can then be introduced into the propellant stream from one

or more marking material inlet ports. The propellant can enter the channel at a high velocity. Alternatively, the propellant can be introduced into the channel at a high pressure, and the channel can include a constriction (for example, de Laval or similar converging/diverging type nozzle) for converting the high pressure of the propellant to high velocity. In such a situation, the propellant is introduced at a port located at a proximal end of the channel (the converging region), and the marking material ports are provided near the distal end of the channel (at or further down-stream of the diverging region), allowing for introduction of marking material into the propellant stream.

In the situation where multiple ports are provided, each port can provide for a different color (for example, cyan, magenta, yellow, and black), pre-marking treatment material (such as a marking material adherent), post-marking treatment material (such as a substrate surface finish material, for example, matte or gloss coating, or the like), marking material not otherwise visible to the unaided eye (for example, magnetic particle-bearing material, ultraviolet-fluorescent material, or the like) or other marking material to be applied to the substrate. Examples of materials suitable for pre-marking treatment and post-marking treatment include polyester resins (either linear or branched); poly(styrenic) homopolymers; poly(acrylate); and poly(methacrylate) homopolymers and mixtures thereof; random copolymers of styrenic monomers with acrylate, methacrylate, or butadiene monomers and mixtures thereof; poly(vinyl acetals); poly(vinyl alcohol)s; vinyl alcohol-vinyl acetal copolymers; polycarbonates; mixtures thereof; and the like. The marking material is imparted with kinetic energy from the propellant stream, and ejected from the channel at an exit orifice located at the distal end of the channel in a direction toward a substrate.

One or more such channels can be provided in a structure which, in one embodiment, is referred to herein as a printhead. The width of the exit (or ejection) orifice of a channel is typically on the order of about 250 microns or smaller, and preferably in the range of about 100 microns or smaller. When more than one channel is provided, the pitch, or spacing from edge to edge (or center to center) between adjacent channels can also be on the order of about 250 microns or smaller, and preferably in the range of about 100 microns or smaller. Alternatively, the channels can be staggered, allowing reduced edge-to-edge spacing. The exit orifice and/or some or all of each channel can have a circular, semicircular, oval, square, rectangular, triangular or other cross-sectional shape when viewed along the direction of flow of the propellant stream (the channel's longitudinal axis).

The marking material to be applied to the substrate can be transported to a port by one or more of a wide variety of ways, including simple gravity feed, hydrodynamic, electrostatic, ultrasonic transport or the like. The material can be metered out of the port into the propellant stream also by one of a wide variety of ways, including control of the transport mechanism, or a separate system such as pressure balancing, electrostatics, acoustic energy, ink jet, or the like.

The marking material to be applied to the substrate can be a solid or semi-solid particulate material, such as a toner or variety of toners in different colors, a suspension of such a marking material in a carrier, a suspension of such a marking material in a carrier with a charge director, a phase change material, or the like. Preferably the marking material is particulate, solid or semi-solid, and dry or suspended in a liquid carrier. Such a marking material is referred to herein as a particulate marking material. A particulate marking

material is to be distinguished from a liquid marking material, dissolved marking material, atomized marking material, or similar non-particulate material, which is generally referred to herein as a liquid marking material. However, ballistic aerosol marking processes are also able to utilize such a liquid marking material in certain applications.

Ballistic aerosol marking processes also enable marking on a wide variety of substrates, including direct marking on non-porous substrates such as polymers, plastics, metals, glass, treated and finished surfaces, and the like. The reduction in wicking and elimination of drying time also provides improved printing to porous substrates such as paper, textiles, ceramics, and the like. In addition, ballistic aerosol marking processes can be configured for indirect marking, such as marking to an intermediate transfer member such as a roller or belt (which optionally can be heated), marking to a viscous binder film and nip transfer system, or the like.

The marking material to be deposited on a substrate can be subjected to post ejection modification, such as fusing or drying, overcoating, curing, or the like. In the case of fusing, the kinetic energy of the material to be deposited can itself be sufficient effectively to melt the marking material upon impact with the substrate and fuse it to the substrate. The substrate can be heated to enhance this process. Pressure rollers can be used to cold-fuse the marking material to the substrate. In-flight phase change (solid-liquid-solid) can alternatively be employed. A heated wire in the particle path is one way to accomplish the initial phase change. Alternatively, propellant temperature can accomplish this result. In one embodiment, a laser can be employed to heat and melt the particulate material in-flight to accomplish the initial phase change. The melting and fusing can also be electrostatically assisted (i.e., retaining the particulate material in a desired position to allow ample time for melting and fusing into a final desired position). The type of particulate can also dictate the post-ejection modification. For example, ultraviolet curable materials can be cured by application of ultraviolet radiation, either in flight or when located on the material-bearing substrate.

Since propellant can continuously flow through a channel, channel clogging from the build-up of material is reduced (the propellant effectively continuously cleans the channel). In addition, a closure can be provided that isolates the channels from the environment when the system is not in use. Alternatively, the printhead and substrate support (for example, a platen) can be brought into physical contact to effect a closure of the channel. Initial and terminal cleaning cycles can be designed into operation of the printing system to optimize the cleaning of the channel(s). Waste material cleaned from the system can be deposited in a cleaning station. It is also possible, however, to engage the closure against an orifice to redirect the propellant stream through the port and into the reservoir thereby to flush out the port.

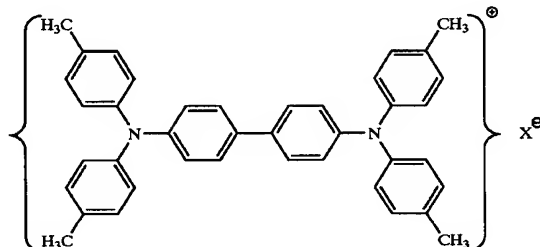
Further details on the ballistic aerosol marking process are disclosed in, for example, application U.S. Ser. No. 09/163,893, now U.S. Pat. No. 6,511,149, filed Sep. 30, 1998, with the named inventors Gregory B. Anderson, Steven B. Bolte, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, Jaan Noolandi, Joel A. Kubby, Eric Peeters, Raj B. Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Ballistic Aerosol Marking Apparatus for Marking a Substrate," Copending application U.S. Ser. No. 09/164,124, now U.S. Pat. No. 6,416,157, filed Sep. 30, 1998, with the named inventors Gregory B. Anderson, Steven B. Bolte, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, Jaan Noolandi, Joel A. Kubby, Eric Peeters, Raj B.

Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Method of Marking a Substrate Employing a Ballistic Aerosol Marking Apparatus," application U.S. Ser. No. 09/164,250, filed Sep. 30, 1998, now issued U.S. Pat. No. 6,340,216, with the named inventors Gregory B. Anderson, Danielle C. Boils, Steven B. Bolte, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, T. Brian McAneney, Maria N. V. McDougall, Karen A. Moffat, Jaan Noolandi, Richard P. N. Veregin, Paul D. Szabo, Joel A. Kubby, Eric Peeters, Raj B. Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Ballistic Aerosol Marking Apparatus for Treating a Substrate," application U.S. Ser. No. 09/163,808, now U.S. Pat. No. 6,523,928, filed Sep. 30, 1998, with the named inventors Gregory B. Anderson, Danielle C. Boils, Steven B. Bolte, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, T. Brian McAneney, Maria N. V. McDougall, Karen A. Moffat, Jaan Noolandi, Richard P. N. Veregin, Paul D. Szabo, Joel A. Kubby, Eric Peeters, Raj B. Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Method of Treating a Substrate Employing a Ballistic Aerosol Marking Apparatus," application U.S. Ser. No. 09/163,765, now U.S. Pat. No. 6,467,862 filed Sep. 30, 1998, with the named inventors Gregory B. Anderson, Steven B. Bolte, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, Jaan Noolandi, Joel A. Kubby, Eric Peeters, Raj B. Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Cartridge for Use in a Ballistic Aerosol Marking Apparatus," application U.S. Ser. No. 09/163,839, now issued U.S. Pat. No. 6,290,342, filed Sep. 30, 1998, with the named inventors Abdul M. Elhatem, Dan A. Hays, Jaan Noolandi, Kaiser H. Wong, Joel A. Kubby, Tuan Anh Vo, and Eric Peeters, entitled "Marking Material Transport," application U.S. Ser. No. 09/163,954, now issued U.S. Pat. No. 6,328,409, filed Sep. 30, 1998, with the named inventors Gregory B. Anderson, Andrew A. Berlin, Steven B. Bolte, Ga Neville Connell, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, Jaan Noolandi, Joel A. Kubby, Eric Peeters, Raj B. Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Ballistic Aerosol Marking Apparatus for Marking with a Liquid Material," application U.S. Ser. No. 09/163,924, now U.S. Pat. No. 6,454,384, filed Sep. 30, 1998, with the named inventors Gregory B. Anderson, Andrew A. Berlin, Steven B. Bolte, Ga Neville Connell, Dan A. Hays, Warren B. Jackson, Gregory J. Kovacs, Meng H. Lean, Jaan Noolandi, Joel A. Kubby, Eric Peeters, Raj B. Apte, Philip D. Floyd, An-Chang Shi, Frederick J. Endicott, Armin R. Volkel, and Jonathan A. Small, entitled "Method for Marking with a Liquid Material Using a Ballistic Aerosol Marking Apparatus," application U.S. Ser. No. 09/163,825, filed Sep. 30, 1998, now U.S. Pat. No. 6,136,442, with the named inventor Kaiser H. Wong, entitled "Multi-Layer Organic Overcoat for Electrode Grid," application U.S. Ser. No. 09/164,104, now U.S. Pat. No. 6,416,156, filed Sep. 30, 1998, with the named inventors T. Brian McAneney, Jaan Noolandi, and An-Chang Shi, entitled "Kinetic Fusing of a Marking Material," application U.S. Ser. No. 09/163,904 (now U.S. Pat. No. 6,116,718), filed Sep. 30, 1998, with the named inventors Meng H. Lean, Jaan Noolandi, Eric Peeters, Raj B. Apte, Philip D. Floyd, and Armin R. Volkel, entitled "Print Head for Use in a Ballistic Aerosol Marking Apparatus," application U.S. Ser. No. 09/163,799, filed Sep. 30, 1998, with the named inventors Meng H. Lean, Jaan

Noolandi, Eric Peeters, Raj B. Apte, Philip D. Floyd, and Armin R. Volkel, entitled "Method of Making a Print Head for Use in a Ballistic Aerosol Marking Apparatus," application U.S. Ser. No. 09/163,664, filed Sep. 30, 1998, now U.S. Pat. No. 6,263,050, with the named inventors Bing R. Hsieh, Kaiser H. Wong, and Tuan Anh Vo, entitled "Organic Overcoat for Electrode Grid," and application U.S. Ser. No. 09/163,518, now issued U.S. Pat. No. 6,291,088, filed Sep. 30, 1998, with the named inventors Kaiser H. Wong and Tuan Anh Vo, entitled "Inorganic Overcoat for Particulate Transport Electrode Grid", the disclosures of each of which are totally incorporated herein by reference.

U.S. Pat. No. 5,834,080 (Mort et al.), the disclosure of which is totally incorporated herein by reference, discloses controllably conductive polymer compositions that may be used in electrophotographic imaging developing systems, such as scavengeless or hybrid scavengeless systems or liquid image development systems. The conductive polymer compositions includes a charge-transporting material (particularly a charge-transporting, thiophene-containing polymer or an inert elastomeric polymer, such as a butadiene- or isoprene-based copolymer or an aromatic polyether-based polyurethane elastomer, that additionally comprises charge transport molecules) and a dopant capable of accepting electrons from the charge-transporting material. The invention also relates to an electrophotographic printing machine, a developing apparatus, and a coated transport member, an intermediate transfer belt, and a hybrid compliant photoreceptor comprising a composition of the invention.

U.S. Pat. No. 5,853,906 (Hsieh), the disclosure of which is totally incorporated herein by reference, discloses a conductive coating comprising an oxidized oligomer salt, a charge transport component, and a polymer binder, for example, a conductive coating comprising an oxidized tetraolydiamine salt of the formula



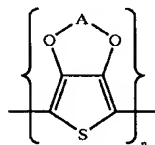
a charge transport component, and a polymer binder, wherein X⁻ is a monovalent anion.

U.S. Pat. No. 5,457,001 (Van Ritter), the disclosure of which is totally incorporated herein by reference, discloses an electrically conductive toner powder, the separate particles of which contain thermoplastic resin, additives conventional in toner powders, such as coloring constituents and possibly magnetically attractable material, and an electrically conductive protonized polyaniline complex, the protonized polyaniline complex preferably having an electrical conductivity of at least 1 S/cm, the conductive complex being distributed over the volume of the toner particles or present in a polymer-matrix at the surface of the toner particles.

U.S. Pat. No. 5,202,211 (Vercoulen et al.), the disclosure of which is totally incorporated herein by reference, discloses a toner powder comprising toner particles which carry on their surface and/or in an edge zone close to the surface

fine particles of electrically conductive material consisting of fluorine-doped tin oxide. The fluorine-doped tin oxide particles have a primary particle size of less than 0.2 micron and a specific electrical resistance of at most 50 ohms.meter. The fluorine content of the tin oxide is less than 10 percent by weight, and preferably is from 1 to 5 percent by weight.

U.S. Pat. No. 5,035,926 (Jonas et al.), the disclosure of which is totally incorporated herein by reference, discloses new polythiophenes containing structural units of the formula



in which A denotes an optionally substituted C_1 - C_4 alkylene radical, their preparation by oxidative polymerization of the corresponding thiophenes, and the use of the polythiophenes for imparting antistatic properties on substrates which only conduct electrical current poorly or not at all, in particular on plastic mouldings, and as electrode material for rechargeable batteries.

While known compositions and processes are suitable for their intended purposes, a need remains for improved marking processes. In addition, a need remains for improved electrostatic imaging processes. Further, a need remains for toners that can be charged inductively and used to develop electrostatic latent images. Additionally, a need remains for toners that can be used to develop electrostatic latent images without the need for triboelectric charging of the toner with a carrier. There is also a need for toners that are sufficiently conductive to be employed in an inductive charging process without being magnetic. In addition, there is a need for conductive, nonmagnetic toners that enable controlled, stable, and predictable inductive charging. Further, there is a need for conductive, nonmagnetic, inductively chargeable toners that enable uniform development of electrostatic images. Additionally, there is a need for conductive, nonmagnetic, inductively chargeable toners that have relatively small average particle diameters (such as 10 microns or less). A need also remains for conductive, nonmagnetic, inductively chargeable toners that have relatively uniform size and narrow particle size distribution values. In addition, a need remains for toners suitable for use in printing apparatus that employ electron beam imaging processes. Further, a need remains for toners suitable for use in printing apparatus that employ single component development imaging processes. Additionally, a need remains for conductive, nonmagnetic, inductively chargeable toners with desirably low melting temperatures. There is also a need for conductive, nonmagnetic, inductively chargeable toners with tunable gloss properties, wherein the same monomers can be used to generate toners that have different melt and gloss characteristics by varying polymer characteristics such as molecular weight (M_w , M_n , M_{WD} , or the like) or crosslinking. In addition, there is a need for conductive, nonmagnetic, inductively chargeable toners that can be prepared by relatively simple and inexpensive methods. Further, there is a need for conductive, nonmagnetic, inductively chargeable toners with desirably glass transition temperatures for enabling efficient transfer of the toner from an intermediate transfer or transfuse member to a print substrate. Additionally, there is a need for conductive, nonmagnetic, inductively chargeable toners with desirably

glass transition temperatures for enabling efficient transfer of the toner from a heated intermediate transfer or transfuse member to a print substrate. A need also remains for conductive, nonmagnetic, inductively chargeable toners that exhibit good fusing performance. In addition, a need remains for conductive, nonmagnetic, inductively chargeable toners that form images with low toner pile heights. Further, a need remains for conductive, nonmagnetic, inductively chargeable toners wherein the toner comprises a resin particle encapsulated with a conductive polymer, wherein the conductive polymer is chemically bound to the particle surface. Additionally, a need remains for conductive, nonmagnetic, inductively chargeable toners that comprise particles having tunable morphology in that the particle shape can be selected to be spherical, highly irregular, or the like. There is also a need for insulative, triboelectrically chargeable toners that enable uniform development of electrostatic images. In addition, there is a need for insulative, triboelectrically chargeable toners that have relatively small average particle diameters (such as 10 microns or less). A need also remains for insulative, triboelectrically chargeable toners that have relatively uniform size and narrow particle size distribution values. In addition, a need remains for insulative, triboelectrically chargeable toners with desirably low melting temperatures. Further, a need remains for insulative, triboelectrically chargeable toners with tunable gloss properties, wherein the same monomers can be used to generate toners that have different melt and gloss characteristics by varying polymer characteristics such as molecular weight (M_w , M_n , M_{WD} , or the like) or crosslinking. Additionally, a need remains for insulative, triboelectrically chargeable toners that can be prepared by relatively simple and inexpensive methods. There is also a need for insulative, triboelectrically chargeable toners with desirably glass transition temperatures for enabling efficient transfer of the toner from an intermediate transfer or transfuse member to a print substrate. In addition, there is a need for insulative, triboelectrically chargeable toners with desirably glass transition temperatures for enabling efficient transfer of the toner from a heated intermediate transfer or transfuse member to a print substrate. Further, there is a need for insulative, triboelectrically chargeable toners that exhibit good fusing performance. Additionally, there is a need for insulative, triboelectrically chargeable toners that form images with low toner pile heights. A need also remains for insulative, triboelectrically chargeable toners wherein the toner comprises a resin particle encapsulated with a polymer, wherein the polymer is chemically bound to the particle surface. In addition, a need remains for insulative, triboelectrically chargeable toners that comprise particles having tunable morphology in that the particle shape can be selected to be spherical, highly irregular, or the like. Further, a need remains for insulative, triboelectrically chargeable toners that can be made to charge either positively or negatively, as desired, without varying the resin or colorant comprising the toner particles. Additionally, a need remains for insulative, triboelectrically chargeable toners that can be made to charge either positively or negatively, as desired, without the need to use or vary surface additives.

SUMMARY OF THE INVENTION

The present invention is directed to a toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process. Another embodiment of the present invention is directed to a process which comprises (a) generating an electrostatic latent image on an imaging

member, and (b) developing the latent image by contacting the imaging member with charged toner particles comprising a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic elevational view of an illustrative electrophotographic printing machine suitable for use with the present invention.

FIG. 2 is a schematic illustration of a development system suitable for use with the present invention.

FIG. 3 illustrates a monolayer of induction charged toner on a dielectric overcoated substrate.

FIG. 4 illustrates a monolayer of previously induction charged toner between donor and receiver dielectric overcoated substrates.

FIG. 5 is a schematic elevational view of an illustrative electrophotographic printing machine incorporating therein a nonmagnetic inductive charging development system for the printing of black and a custom color.

FIG. 6 is a schematic illustration of a ballistic aerosol marking system for marking a substrate according to the present invention.

FIG. 7 is cross sectional illustration of a ballistic aerosol marking apparatus according to one embodiment of the present invention.

FIG. 8 is another cross sectional illustration of a ballistic aerosol marking apparatus according to one embodiment of the present invention.

FIG. 9 is a plan view of one channel, with nozzle, of the ballistic aerosol marking apparatus shown in FIG. 8.

FIGS. 10A through 10C and 11A through 11C are end views, in the longitudinal direction, of several examples of channels for a ballistic aerosol marking apparatus.

FIG. 12 is another plan view of one channel of a ballistic aerosol marking apparatus, without a nozzle, according to the present invention.

FIGS. 13A through 13D are end views, along the longitudinal axis, of several additional examples of channels for a ballistic aerosol marking apparatus.

DETAILED DESCRIPTION OF THE INVENTION

Marking materials of the present invention can be used in conventional electrostatic imaging processes, such as electrophotography, ionography, electrography, or the like. Another embodiment of the present invention is directed to a process which comprises (a) generating an electrostatic latent image on an imaging member, and (b) developing the latent image by contacting the imaging member with charged toner particles according to the present invention. In one embodiment of the present invention, the toner particles are charged triboelectrically, in either a single component development process or a two-component development process. In another embodiment of the present invention, the toner particles are charged by an inductive charging process. In one specific embodiment employing inductive charging, the developing apparatus comprises a housing defining a reservoir storing a supply of developer material comprising the conductive toner; a donor member for transporting toner on an outer surface of said donor member to a development zone; means for loading a toner layer onto said outer surface of said donor member; and means for inductive charging

said toner layer onto said outer surface of said donor member prior to the development zone to a predefined charge level. In a particular embodiment, the inductive charging means comprises means for biasing the toner reservoir relative to the bias on the donor member. In another particular embodiment, the developing apparatus further comprises means for moving the donor member into synchronous contact with the imaging member to detach toner in the development zone from the donor member, thereby developing the latent image. In yet another specific embodiment, the predefined charge level has an average toner charge-to-mass ratio of from about 5 to about 50 microCoulombs per gram in magnitude. Yet another specific embodiment of the present invention is directed to a process for developing a latent image recorded on a surface of an image receiving member to form a developed image, said process comprising (a) moving the surface of the image receiving member at a predetermined process speed; (b) storing in a reservoir a supply of toner particles according to the present invention; (c) transporting the toner particles on an outer surface of a donor member to a development zone adjacent the image receiving member; and (d) inductive charging said toner particles on said outer surface of said donor member prior to the development zone to a predefined charge level. In a particular embodiment, the inductive charging step includes the step of biasing the toner reservoir relative to the bias on the donor member. In another particular embodiment, the donor member is brought into synchronous contact with the imaging member to detach toner in the development zone from the donor member, thereby developing the latent image. In yet another particular embodiment, the predefined charge level has an average toner charge-to-mass ratio of from about 5 to about 50 microCoulombs per gram in magnitude.

In some embodiments of these processes, the marking material can comprise toner particles that are relatively insulative for use with triboelectric charging processes, with average bulk conductivity values typically of no more than about 10^{-12} Siemens per centimeter, and preferably no more than about 10^{-13} Siemens per centimeter, and with conductivity values typically no less than about 10^{-16} Siemens per centimeter, and preferably no less than about 10^{-15} Siemens per centimeter, although the conductivity values can be outside of these ranges. "Average bulk conductivity" refers to the ability for electrical charge to pass through a pellet of the particles, measured when the pellet is placed between two electrodes. The particle conductivity can be adjusted by various synthetic parameters of the polymerization; reaction time, molar ratios of oxidant and dopant to pyrrole monomer, temperature, and the like. These insulative toner particles are charged triboelectrically and used to develop the electrostatic latent image.

In embodiments of the present invention in which the marking particles are used in electrostatic imaging processes wherein the marking particles are triboelectrically charged, toners of the present invention can be employed alone in single component development processes, or they can be employed in combination with carrier particles in two component development processes. Any suitable carrier particles can be employed with the toner particles. Typical carrier particles include granular zircon, steel, nickel, iron ferrites, and the like. Other typical carrier particles include nickel berry carriers as disclosed in U.S. Pat. No. 3,847,604, the entire disclosure of which is incorporated herein by reference. These carriers comprise nodular carrier beads of nickel characterized by surfaces of reoccurring recesses and protrusions that provide the particles with a relatively large

external area. The diameters of the carrier particles can vary, but are generally from about 30 microns to about 1,000 microns, thus allowing the particles to possess sufficient density and inertia to avoid adherence to the electrostatic images during the development process.

Carrier particles can possess coated surfaces. Typical coating materials include polymers and terpolymers, including, for example, fluoropolymers such as polyvinylidene fluorides as disclosed in U.S. Pat. No. 3,526,533, U.S. Pat. No. 3,849,186, and U.S. Pat. No. 3,942,979, the disclosures of each of which are totally incorporated herein by reference. Coating of the carrier particles may be by any suitable process, such as powder coating, wherein a dry powder of the coating material is applied to the surface of the carrier particle and fused to the core by means of heat, solution coating, wherein the coating material is dissolved in a solvent and the resulting solution is applied to the carrier surface by tumbling, or fluid bed coating, in which the carrier particles are blown into the air by means of an air stream, and an atomized solution comprising the coating material and a solvent is sprayed onto the airborne carrier particles repeatedly until the desired coating weight is achieved. Carrier coatings may be of any desired thickness or coating weight. Typically, the carrier coating is present in an amount of from about 0.1 to about 1 percent by weight of the uncoated carrier particle, although the coating weight may be outside this range.

In a two-component developer, the toner is present in the developer in any effective amount, typically from about 1 to about 10 percent by weight of the carrier, and preferably from about 3 to about 6 percent by weight of the carrier, although the amount can be outside these ranges.

Any suitable conventional electrophotographic development technique can be utilized to deposit toner particles of the present invention on an electrostatic latent image on an imaging member. Well known electrophotographic development techniques include magnetic brush development, cascade development, powder cloud development, and the like. Magnetic brush development is more fully described, for example, in U.S. Pat. No. 2,791,949, the disclosure of which is totally incorporated herein by reference; cascade development is more fully described, for example, in U.S. Pat. No. 2,618,551 and U.S. Pat. No. 2,618,552, the disclosures of each of which are totally incorporated herein by reference; powder cloud development is more fully described, for example, in U.S. Pat. No. 2,725,305, U.S. Pat. No. 2,918,910, and U.S. Pat. No. 3,015,305, the disclosures of each of which are totally incorporated herein by reference.

In other embodiments of the present invention wherein nonmagnetic inductive charging methods are employed, the marking material can comprise toner particles that are relatively conductive, with average bulk conductivity values typically of no less than about 10^{-11} Siemens per centimeter, and preferably no less than about 10^{-7} Siemens per centimeter, although the conductivity values can be outside of these ranges. There is no upper limit on conductivity for these embodiments of the present invention. "Average bulk conductivity" refers to the ability for electrical charge to pass through a pellet of the particles, measured when the pellet is placed between two electrodes. The particle conductivity can be adjusted by various synthetic parameters of the polymerization; reaction time, molar ratios of oxidant and dopant to pyrrole monomer, temperature, and the like. These conductive toner particles are charged by a nonmagnetic inductive charging process and used to develop the electrostatic latent image.

While the present invention will be described in connection with a specific embodiment thereof, it will be under-

stood that it is not intended to limit the invention to that embodiment. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

Inasmuch as the art of electrophotographic printing is well known, the various processing stations employed in the printing machine of FIG. 1 will be shown hereinafter schematically and their operation described briefly with reference thereto.

Referring initially to FIG. 1, there is shown an illustrative electrostatographic printing machine. The printing machine, in the shown embodiment an electrophotographic printer (although other printers are also suitable, such as ionographic printers and the like), incorporates a photoreceptor 10, in the shown embodiment in the form of a belt (although other known configurations are also suitable, such as a roll, a drum, a sheet, or the like), having a photoconductive surface layer 12 deposited on a substrate. The substrate can be made from, for example, a polyester film such as MYLAR® that has been coated with a thin conductive layer which is electrically grounded. The belt is driven by means of motor 54 along a path defined by rollers 49, 51, and 52, the direction of movement being counterclockwise as viewed and as shown by arrow 16. Initially a portion of the belt 10 passes through a charge station A at which a corona generator 48 charges surface 12 to a relatively high, substantially uniform, potential. A high voltage power supply 50 is coupled to device 48.

Next, the charged portion of photoconductive surface 12 is advanced through exposure station B. In the illustrated embodiment, at exposure station B, a Raster Output Scanner (ROS) 56 scans the photoconductive surface in a series of scan lines perpendicular to the process direction. Each scan line has a specified number of pixels per inch. The ROS includes a laser with a rotating polygon mirror to provide the scanning perpendicular to the process direction. The ROS imagewise exposes the charged photoconductive surface 12. Other methods of exposure are also suitable, such as light lens exposure of an original document or the like.

After the electrostatic latent image has been recorded on photoconductive surface 12, belt 10 advances the latent electrostatic image to development station C as shown in FIG. 1. At development station C, a development system or developer unit 44 develops the latent image recorded on the photoconductive surface. The chamber in the developer housing stores a supply of developer material. In embodiments of the present invention in which the developer material comprises insulative toner particles that are triboelectrically charged, either two component development, in which the developer comprises toner particles and carrier particles, or single component development, in which only toner particles are used, can be selected for developer unit 44. In embodiments of the present invention in which the developer material comprises conductive or semiconductive toner particles that are inductively charged, the developer material is a single component developer consisting of nonmagnetic, conductive toner that is induction charged on a dielectric overcoated donor roll prior to the development zone. The developer material may be a custom color consisting of two or more different colored dry powder toners.

Again referring to FIG. 1, after the electrostatic latent image has been developed, belt 10 advances the developed image to transfer station D. Transfer can be directly from the imaging member to a receiving sheet or substrate, such as paper, transparency, or the like, or can be from the imaging

member to an intermediate and subsequently from the intermediate to the receiving sheet or substrate. In the illustrated embodiment, at transfer station D, the developed image is tack transferred to a heated transfuse belt or roll 100. The covering on the compliant belt or drum typically consists of a thick (1.3 millimeter) soft (IRHD hardness of about 40) silicone rubber. (Thinner and harder rubbers provide tradeoffs in latitudes. The rubber can also have a thin VITON® top coat for improved reliability.) If the transfuse belt or roll is maintained at a temperature near 120° C., tack transfer of the toner from the photoreceptor to the transfuse belt or drum can be obtained with a nip pressure of about 50 pounds per square inch. As the toned image advances from the photoreceptor-transfuse belt nip to the transfuse belt-medium transfuse nip formed between transfuse belt 100 and roller 68, the toner is softened by the ~120° C. transfuse belt temperature. With the receiving sheet 64 preheated to about 85° C. in guides 66 by a heater 200, as receiving sheet 64 is advanced by roll 62 and guides 66 into contact with the developed image on roll 100, transfuse of the image to the receiving sheet is obtained with a nip pressure of about 100 pounds per square inch. It should be noted that the toner release from the roll 100 can be aided by a small amount of silicone oil that is imbibed in the roll for toner release at the toner/roll interface. The bulk of the compliant silicone material also contains a conductive carbon black to dissipate any charge accumulation. As noted in FIG. 1, a cleaner 210 for the transfuse belt material is provided to remove residual toner and fiber debris. An optional glossing station (not shown) can be employed by the customer to select a desired image gloss level.

After the developed image has been transferred from photoconductive surface 12 of belt 10, the residual developer material adhering to photoconductive surface 12 is removed therefrom by a rotating fibrous brush 78 at cleaning station E in contact with photoconductive surface 12. Subsequent to cleaning, a discharge lamp (not shown) floods photoconductive surface 12 with light to dissipate any residual electrostatic charge remaining thereon prior to the charging thereof for the next successive imaging cycle.

Referring now to FIG. 2, which illustrates a specific embodiment of the present invention in which the toner in housing 44 is inductively charged, as the donor 42 rotates in the direction of arrow 69, a voltage DC_D 300 is applied to the donor roll to transfer electrostatically the desired polarity of toner to the belt 10 while at the same time preventing toner transfer in the nonimage areas of the imaged belt 10. Donor roll 42 is mounted, at least partially, in the chamber of developer housing 44 containing nonmagnetic conductive toner. The chamber in developer housing 44 stores a supply of the toner that is in contact with donor roll 42. Donor roll 42 can be, for example, a conductive aluminum core overcoated with a thin (50 micron) dielectric insulating layer. A voltage DC_L 302 applied between the developer housing 44 and the donor roll 42 causes induction charging and loading of the nonmagnetic conductive toner onto the dielectric overcoated donor roll.

As successive electrostatic latent images are developed, the toner particles within the developer housing 44 are depleted. A toner dispenser (not shown) stores a supply of toner particles. The toner dispenser is in communication with housing 44. As the level of toner particles in the chamber is decreased, fresh toner particles are furnished from the toner dispenser.

The maximum loading of induction charged, conductive toner onto the dielectric overcoated donor roll 42 is preferably limited to approximately a monolayer of toner. For a

voltage DC_L 302 greater than approximately 100 volts, the monolayer loading is essentially independent of bias level. The charge induced on the toner monolayer, however, is proportional to the voltage DC_L 302. Accordingly, the charge-to-mass ratio of the toner loaded on donor roll 42 can be controlled according to the voltage DC_L 302. As an example, if a DC_L voltage of ~200 volts is applied to load conductive toner onto donor roll 42 with a dielectric overcoating thickness of 25 microns, the toner charge-to-mass ratio is ~17 microCoulombs per gram.

As the toned donor rotates in the direction indicated by arrow 69 in FIG. 2, it is desirable to condition the toner layer on the donor roll 42 before the development zone 310. The objective of the toner layer conditioning device is to remove any toner in excess of a H monolayer. Without the toner layer conditioning device, toner-toner contacts in the development zone can cause wrong-sign toner generation and deposition in the nonimage areas. A toner layer conditioning device 400 is illustrated in FIG. 2. This particular example uses a compliant overcoated roll that is biased at a voltage DC_C 304. The overcoating material is charge relaxable to enable dissipation of any charge accumulation. The voltage DC_C 304 is set at a higher magnitude than the voltage DC_L 302. For synchronous contact between the donor roll 42 and conditioning roll 400 under the bias voltage conditions, any toner on donor roll 42 that is on top of toner in the layer is induction charged with opposite polarity and deposited on the roll 400. A doctor blade on conditioning roll 400 continually removes the deposited toner.

As donor 42 is rotated further in the direction indicated by arrow 69, the now induction charged and conditioned toner layer is moved into development zone 310, defined by a synchronous contact between donor 42 and the photoreceptor belt 10. In the image areas, the toner layer on the donor roll is developed onto the photoreceptor by electric fields created by the latent image. In the nonimage areas, the electric fields prevent toner deposition. Since the adhesion of induction charged, conductive toner is typically less than that of triboelectrically charged toner, only DC electric fields are required to develop the latent electrostatic image in the development zone. The DC field is provided by both the DC voltages DC_D 300 and DC_L 302, and the electrostatic potentials of the latent image on photoconductor 10.

Since the donor roll 42 is overcoated with a highly insulative material, undesired charge can accumulate on the overcoating surface over extended development system operation. To eliminate any charge accumulation, a charge neutralizing device may be employed. One example of such device is illustrated in FIG. 2 whereby a rotating electrostatic brush 315 is brought into contact with the toned donor roll. The voltage on the brush 315 is set at or near the voltage applied to the core of donor roll 42.

An advantageous feature of nonmagnetic inductive charging is that the precharging of conductive, nonmagnetic toner prior to the development zone enables the application of an electrostatic force in the development zone for the prevention of background toner and the deposition of toner in the image areas. Background control and image development with an induction charged, nonmagnetic toner employs a process for forming a monolayer of toner that is brought into contact with an electrostatic image. Monolayer toner coverage is sufficient in providing adequate image optical density if the coverage is uniform. Monolayer coverage with small toner enables thin images desired for high image quality.

To understand how toner charge is controlled with non-magnetic inductive charging, FIG. 3 illustrates a monolayer

of induction charged toner on a dielectric overcoated substrate 42. The monolayer of toner is deposited on the substrate when a voltage V_A is applied to conductive toner. The average charge density on the monolayer of induction charged toner is given by the formula

$$\sigma = \frac{V_A \epsilon_0}{(T_d / \kappa_d + 0.32 R_p)} \quad (1)$$

where T_d is the thickness of the dielectric layer, κ_d is the dielectric constant, R_p is the particle radius, and ϵ_0 is the permittivity of free space. The $0.32R_p$ term (obtained from empirical studies) describes the average dielectric thickness of the air space between the monolayer of conductive particles and the insulative layer.

For a 25 micron thick dielectric layer ($\kappa_d=3.2$), toner radius of 6.5 microns, and applied voltage of -200 volts, the calculated surface charge density is -18 nC/cm². Since the toner mass density for a square lattice of 13 micron nonmagnetic toner is about 0.75 mg/cm², the toner charge-to-mass ratio is about -17 microCoulombs per gram. Since the toner charge level is controlled by the induction charging voltage and the thickness of the dielectric layer, one can expect that the toner charging will not depend on other factors such as the toner pigment, flow additives, relative humidity, or the like.

With an induction charged layer of toner formed on a donor roll or belt, the charged layer can be brought into contact with an electrostatic image on a dielectric receiver. FIG. 4 illustrates an idealized situation wherein a monolayer of previously induction charged conductive spheres is sandwiched between donor 42 and receiver dielectric materials 10.

The force per unit area acting on induction charged toner in the presence of an applied field from a voltage difference, V_o , between the donor and receiver conductive substrates is given by the equation

$$F/A = \frac{\sigma^2}{2\epsilon_0} \left(\frac{T_r/K_r + T_o^r - T_d/K_d - T_o^d}{T_r/K_r + T_d/K_d + T_o^r + T_o^d} \right) + \frac{\sigma V_o}{T_r/K_r + T_d/K_d + T_o^r + T_o^d} - (F_{sr}^d - F_{sr}^r)$$

where σ is the average charge density on the monolayer of induction charged toner (described by Equation 1), T_r/κ_r and T_d/κ_d are the dielectric thicknesses of the receiver and donor, respectively, T_o^r and T_o^d are the average thicknesses of the receiver and donor air gaps, respectively, V_o is the applied potential, $T_o=0.32 R_p$ where R_p is the particle radius, ϵ_0 is the permittivity of free space, and F_{sr}^r and F_{sr}^d are the short-range force per unit area at the receiver and donor interfaces, respectively. The first term, because of an electrostatic image force from neighboring particles, becomes zero when the dielectric thicknesses of the receiver and its air gap are equal to the dielectric thicknesses of the donor and its air gap. Under these conditions, the threshold applied voltage for transferring toner to the receiver should be zero if the difference in the receiver and donor short-range forces is negligible. One expects, however, a distribution in the short-range forces.

To illustrate the functionality of the nonmagnetic inductive charging device, the developer system of FIG. 2 was tested under the following conditions. A sump of toner (conducting toner of 13 micron volume average particle size) biased at a potential of -200 volts was placed in contact with a 25 micron thick MYLAR® (grounded aluminum on

backside) donor belt moving at a speed of 4.2 inches per second. To condition the toner layer and to remove any loosely adhering toner, a 25 micron thick MYLAR® covered aluminum roll was biased at a potential of -300 volts and contacted with the toned donor belt at substantially the same speed as the donor belt. This step was repeated a second time. The conditioned toner layer was then contacted to an electrostatic image moving at substantially the same speed as the toned donor belt. The electrostatic image had a potential of -650 volts in the nonimage areas and -200 volts in the image areas. A DC potential of +400 volts was applied to the substrate of electrostatic image bearing member during synchronous contact development. A toned image with adequate optical density and low background was observed.

Nonmagnetic inductive charging systems based on induction charging of conductive toner prior to the development zone offer a number of advantages compared to electrophotographic development systems based on triboelectric charging of insulative toner. The toner charging depends only on the induction charging bias, provided that the toner conductivity is sufficiently high. Thus, the charging is insensitive to toner materials such as pigment and resin. Furthermore, the performance should not depend on environmental conditions such as relative humidity.

Nonmagnetic inductive charging systems can also be used in electrographic printing systems for printing black plus one or several separate custom colors with a wide color gamut obtained by blending multiple conductive, nonmagnetic color toners in a single component development system. The induction charging of conductive toner blends is generally pigment-independent. Each electrostatic image is formed with either ion or Electron Beam Imaging (EBI) and developed on separate electroreceptors. The images are tack transferred image-next-to-image onto a transfuse belt or drum for subsequent heat and pressure transfuse to a wide variety of media. The custom color toners, including metallics, are obtained by blending different combinations and percentages of toners from a set of nine primary toners plus transparent and black toners to control the lightness or darkness of the custom color. The blending of the toners can be done either outside of the electrophotographic printing system or within the system, in which situation the different proportions of color toners are directly added to the in-situ toner dispenser.

FIG. 5 illustrates the components and architecture of such a system for custom color printing. FIG. 5 illustrates two electroreceptor modules, although it is understood that additional modules can be included for the printing of multiple custom colors on a document. For discussion purposes, it is assumed that the second module 2 prints black toner. The electroreceptor module 2 uses a nonmagnetic, conductive toner single component development (SCD) system that has been described in FIG. 2. A conventional SCD system, however, that uses magnetic, conductive toner that is induction charged by the electrostatic image on the electroreceptor can also be used to print the black toner.

For the electroreceptor module 1 for the printing of custom color, an electrostatic image is formed on an electroreceptor drum 505 with either ion or Electron Beam Imaging device 510 as taught in U.S. Pat. No. 5,039,598, the disclosure of which is totally incorporated herein by reference. The nonmagnetic, single component development system contains a blend of nonmagnetic, conductive toners to produce a desired custom color. An insulative overcoated donor 42 is loaded with the induction charged blend of toners. A toner layer conditioning station 400 helps to ensure

a monolayer of induction charged toner on the donor. (Monolayer toner coverage is sufficient to provide adequate image optical density if the coverage is uniform. Monolayer coverage with small toner particles enables thin images desired for high image quality.) The monolayer of induction charged toner on the donor is brought into synchronous contact with the imaged electroreceptor **505**. (The development system assembly can be cammed in and out so that it is only in contact with warmer electroreceptor during copying/printing.) The precharged toner enables the application of an electrostatic force in the development zone for the prevention of background toner and the deposition of toner in the image areas. The toned image on the electroreceptor is tack transferred to the heated transfuse member **100** which can be a belt or drum. The covering on the compliant transfuse belt or drum typically consists of a thick (1.3 millimeter) soft (IRHD hardness of about 40) silicone rubber. Thinner and harder rubbers can provide tradeoffs in latitudes. The rubber can also have a thin VITON® top coat for improved reliability. If the transfuse belt/drum is maintained at a temperature near 120° C., tack transfer of the toner from the electroreceptor to the transfuse belt/drum can be obtained with a nip pressure of about 50 psi. As the toned image advances from the electroreceptor-transfuse drum nip for each module to the transfuse drum-medium transfuse nip, the toner is softened by the about 1200C transfuse belt temperature. With the medium **64** (paper for purposes of this illustrative discussion although others can also be used) preheated by heater **200** to about 85° C., transfuse of the image to the medium is obtained with a nip pressure of about 100 psi. The toner release from the silicone belt can be aided by a small amount of silicone oil that is imbibed in the belt for toner release at the toner/belt interface. The bulk of the compliant silicone material also contains a conductive carbon black to dissipate any charge accumulation. As noted in FIG. 5, a cleaner **210** for the transfuse drum material is provided to remove residual toner and fiber debris. An optional glossing station **610** enables the customer to select a desired image gloss level. The electroreceptor cleaner **514** and erase bar **512** are provided to prepare for the next imaging cycle.

The illustrated black plus custom color(s) printing system enables improved image quality through the use of smaller toners (3 to 10 microns), such as toners prepared by an emulsion aggregation process.

The SCD system for module **1** shown in FIG. 5 inherently can have a small sump of toner, which is advantageous in switching the custom color to be used in the SCD system. The bulk of the blended toner can be returned to a supply bottle of the particular blend. The residual toner in the housing can be removed by vacuuming **700**. SCD systems are advantaged compared to two-component developer systems, since in two-component systems the toner must be separated from the carrier beads if the same beads are to be used for the new custom color blend.

A particular custom color can be produced by offline equipment that blends a number of toners selected from a set of nine primary color toners (plus transparent and black toners) that enable a wide custom color gamut, such as PANTONE® colors. A process for selecting proportional amounts of the primary toners for in-situ addition to a SCD housing can be provided by dispenser **600**. The color is controlled by the relative weights of primaries. The $P_1 \dots P_N$ primaries can be selected to dispense toner into a toner bottle for feeding toner to a SCD housing in the machine, or to dispense directly to the sump of the SCD system on a periodic basis according to the amount needed based on the

run length and area coverage. The dispensed toners are tumbled/agitated to blend the primary toners prior to use. In addition to the nine primary color toners for formulating a wide color gamut, one can also use metallic toners (which tend to be conducting and therefore compatible with the SCD process) which are desired for greeting, invitation, and name card applications. Custom color blends of toner can be made in an offline (paint shop) batch process; one can also arrange to have a set of primary color toners continuously feeding a sump of toner within (in-situ) the printer, which enables a dial-a-color system provided that an in-situ toner waste system is provided for color switching.

The deposited toner image can be transferred to a receiving member such as paper or transparency material by any suitable technique conventionally used in electrophotography, such as corona transfer, pressure transfer, adhesive transfer, bias roll transfer, and the like. Typical corona transfer entails contacting the deposited toner particles with a sheet of paper and applying an electrostatic charge on the side of the sheet opposite to the toner particles. A single wire corotron having applied thereto a potential of between about 5000 and about 8000 volts provides satisfactory transfer. The developed toner image can also first be transferred to an intermediate transfer member, followed by transfer from the intermediate transfer member to the receiving member.

After transfer, the transferred toner image can be fixed to the receiving sheet. The fixing step can be also identical to that conventionally used in electrophotographic imaging. Typical, well known electrophotographic fusing techniques include heated roll fusing, flash fusing, oven fusing, laminating, adhesive spray fixing, and the like. Transfix or transfuse methods can also be employed, in which the developed image is transferred to an intermediate member and the image is then simultaneously transferred from the intermediate member and fixed or fused to the receiving member.

The marking materials of the present invention are also suitable for use in ballistic aerosol marking processes. In the following detailed description, numeric ranges are provided for various aspects of the embodiments described, such as pressures, velocities, widths, lengths, and the like. These recited ranges are to be treated as examples only, and are not intended to limit the scope of the claims hereof. In addition, a number of materials are identified as suitable for various aspects of the embodiments, such as for marking materials, propellants, body structures, and the like. These recited materials are also to be treated as exemplary, and are not intended to limit the scope of the claims hereof.

With reference now to FIG. 6, shown therein is a schematic illustration of a ballistic aerosol marking device **110** according to one embodiment of the present invention. As shown therein, device **110** comprises one or more ejectors **112** to which a propellant **114** is fed. A marking material **116**, which can be transported by a transport **118** under the command of control **120**, is introduced into ejector **112**. (Optional elements are indicated by dashed lines.) The marking material is metered (that is controllably introduced) into the ejector by metering device **121**, under command of control **122**. The marking material ejected by ejector **112** can be subject to post-ejection modification **123**, optionally also part of device **110**. Each of these elements will be described in further detail below. It will be appreciated that device **110** can form a part of a printer, for example of the type commonly attached to a computer network, personal computer or the like, part of a facsimile machine, part of a document duplicator, part of a labelling apparatus, or part of any other of a wide variety of marking devices.

The embodiment illustrated in FIG. 6 can be realized by a ballistic aerosol marking device 124 of the type shown in the cut-away side view of FIG. 7. According to this embodiment, the materials to be deposited will be four colored marking materials, for example cyan (C), magenta (M), yellow (Y), and black (K), of a type described further herein, which can be deposited concomitantly, either mixed or unmixed, successively, or otherwise. While the illustration of FIG. 7 and the associated description contemplates a device for marking with four colors (either one color at a time or in mixtures thereof), a device for marking with a fewer or a greater number of colors, or other or additional materials, such as materials creating a surface for adhering marking material particles (or other substrate surface pretreatment), a desired substrate finish quality (such as a matte, satin or gloss finish or other substrate surface post-treatment), material not visible to the unaided eye (such as magnetic particles, ultra violet-fluorescent particles, and the like) or other material associated with a marked 193 substrate, is clearly contemplated herein.

Device 124 comprises a body 126 within which is formed a plurality of cavities 128C, 128M, 128Y, and 128K (collectively referred to as cavities 128) for receiving materials to be deposited. Also formed in body 126 can be a propellant cavity 130. A fitting 132 can be provided for connecting propellant cavity 130 to a propellant source 133 such as a compressor, a propellant reservoir, or the like.

With reference now to FIG. 8, shown therein is a cut-away cross section of a portion of device 124. Body 126 can be connected to a print head 134, comprising, among other layers, substrate 136 and channel layer 137. Each of cavities 128 include a port 142C, 142M, 142Y, and 142K (collectively referred to as ports 142) respectively, of circular, oval, rectangular, or other cross-section, providing communication between said cavities, and a channel 146 which adjoins body 126. Ports 142 are shown having a longitudinal axis roughly perpendicular to the longitudinal axis of channel 146. The angle between the longitudinal axes of ports 142 and channel 146, however, can be other than 90 degrees, as appropriate for the particular application of the present invention.

Likewise, propellant cavity 130 includes a port 144, of circular, oval, rectangular, or other cross-section, between said cavity and channel 146 through which propellant can travel. Alternatively, print head 134 can be provided with a port 144' in substrate 136 or port 144" in channel layer 137, or combinations thereof, for the introduction of propellant into channel 146. As will be described further below, marking material is caused to flow out from cavities 128 through ports 142 and into a stream of propellant flowing through channel 146. The marking material and propellant are directed in the direction of arrow AA toward a substrate 138, for example paper, supported by a platen 140, as shown in FIG. 7. It has been demonstrated that a propellant marking material flow pattern from a print head employing a number of the features described herein can remain relatively collimated for a distance of up to 10 millimeters, with an optimal printing spacing on the order of between one and several millimeters. For example, the print head can produce a marking material stream which does not deviate by more than about 20 percent, and preferably by not more than about 10 percent, from the width of the exit orifice for a distance of at least 4 times the exit orifice width. The appropriate spacing between the print head and the substrate, however, is a function of many parameters, and does not itself form a part of the present invention. In one preferred embodiment, the kinetic energy of the particles, which are moving at very

high velocities toward the substrate, is converted to thermal energy upon impact of the particles on the substrate, thereby fixing or fusing the particles to the substrate. In this embodiment, the glass transition temperature of the resin in the particles is selected so that the thermal energy generated by impact with the substrate is sufficient to fuse the particles to the substrate; this process is called kinetic fusing.

According to one embodiment of the present invention, print head 134 comprises a substrate 136 and channel layer 137 in which is formed channel 146. Additional layers, such as an insulating layer, capping layer, or the like (not shown) can also form a part of print head 134. Substrate 136 is formed of a suitable material such as glass, ceramic, or the like, on which (directly or indirectly) is formed a relatively thick material, such as a thick permanent photoresist (for example, a liquid photosensitive epoxy such as SU-8, commercially available from Microlithography Chemicals, Inc.; see also U.S. Pat. No. 4,882,245, the disclosure of which is totally incorporated herein by reference) and/or a dry film-based photoresist such as the Riston photopolymer resist series, commercially available from DuPont Printed Circuit Materials, Research Triangle Park, N.C. which can be etched, machined, or otherwise in which can be formed a channel with features described below.

Referring now to FIG. 9, which is a cut-away plan view of print head 134, in one embodiment channel 146 is formed to have at a first, proximal end a propellant receiving region 147, an adjacent converging region 148, a diverging region 150, and a marking material injection region 152. The point of transition between the converging region 148 and diverging region 150 is referred to as throat 153, and the converging region 148, diverging region 150, and throat 153 are collectively referred to as a nozzle. The general shape of such a channel is sometimes referred to as a de Laval expansion pipe or a venturi convergence/divergence structure. An exit orifice 156 is located at the distal end of channel 146.

In the embodiment of the present invention shown in FIGS. 8 and 9, region 148 converges in the plane of FIG. 9, but not in the plane of FIG. 8, and likewise region 150 diverges in the plane of FIG. 9, but not in the plane of FIG. 8. Typically, this divergence determines the cross-sectional shape of the exit orifice 156. For example, the shape of orifice 156 illustrated in FIG. 10A corresponds to the device shown in FIGS. 8 and 9. However, the channel can be fabricated such that these regions converge/diverge in the plane of FIG. 8, but not in the plane of FIG. 9 (illustrated in FIG. 10B), or in both the planes of FIGS. 8 and 9 (illustrated in FIG. 10C), or in some other plane or set of planes, or in all planes (examples illustrated in FIGS. 11A-11C) as can be determined by the manufacture and application of the present invention.

In another embodiment, shown in FIG. 12, channel 146 is not provided with a converging and diverging region, but rather has a uniform cross section along its axis. This cross section can be rectangular or square (illustrated in FIG. 13A), oval or circular (illustrated in FIG. 13B), or other cross section (examples are illustrated in FIGS. 13C-13D), as can be determined by the manufacture and application of the present invention.

Any of the aforementioned channel configurations or cross sections are suitable for the present invention. The de Laval or venturi configuration is, however, preferred because it minimizes spreading of the collimated stream of marking particles exiting the channel.

Referring again to FIG. 8, propellant enters channel 146 through port 144, from propellant cavity 130, roughly per-

pendicular to the long axis of channel 146. According to another embodiment, the propellant enters the channel parallel (or at some other angle) to the long axis of channel 146 by, for example, ports 144' or 144" or other manner not shown. The propellant can flow continuously through the channel while the marking apparatus is in an operative configuration (for example, a "power on" or similar state ready to mark), or can be modulated such that propellant passes through the channel only when marking material is to be ejected, as dictated by the particular application of the present invention. Such propellant modulation can be accomplished by a valve 131 interposed between the propellant source 133 and the channel 146, by modulating the generation of the propellant for example by turning on and off a compressor or selectively initiating a chemical reaction designed to generate propellant, or the like.

Marking material can controllably enter the channel through one or more ports 142 located in the marking material injection region 152. That is, during use, the amount of marking material introduced into the propellant stream can be controlled from zero to a maximum per spot. The propellant and marking material travel from the proximal end to a distal end of channel 146 at which is located exit orifice 156.

According to one embodiment for metering the marking material, the marking material includes material which can be imparted with an electrostatic charge. For example, the marking material can comprise a pigment suspended in a binder together with charge directors. The charge directors can be charged, for example by way of a corona 166C, 166M, 166Y, and 166K (collectively referred to as coronas 166), located in cavities 128, shown in FIG. 8. Another option is initially to charge the propellant gas, for example, by way of a corona 145 in cavity 130 (or some other appropriate location such as port 144 or the like.) The charged propellant can be made to enter into cavities 128 through ports 142, for the dual purposes of creating a fluidized bed 186C, 186M, 186Y, and 186K (collectively referred to as fluidized bed 186), and imparting a charge to the marking material. Other options include tribocharging, by other means external to cavities 128, or other mechanism.

Formed at one surface of channel 146, opposite each of the ports 142 are electrodes 154C, 154M, 154Y, and 154K (collectively referred to as electrodes 154). Formed within cavities 128 (or some other location such as at or within ports 144) are corresponding counter-electrodes 155C, 155M, 155Y, and 155K (collectively referred to as counter-electrodes 155). When an electric field is generated by electrodes 154 and counter-electrodes 155, the charged marking material can be attracted to the field, and exits cavities 128 through ports 142 in a direction roughly perpendicular to the propellant stream in channel 146. Alternatively, when an electric field is generated by electrodes 154 and counter-electrodes 155, a charge can be induced on the marking material, provided that the marking material has sufficient conductivity, and can be attracted to the field, and exits cavities 128 through ports 142 in a direction roughly perpendicular to the propellant stream in channel 146. In either embodiment, the shape and location of the electrodes and the charge applied thereto determine the strength of the electric field, and accordingly determine the force of the injection of the marking material into the propellant stream. In general, the force injecting the marking material into the propellant stream is chosen such that the momentum provided by the force of the propellant stream on the marking material overcomes the injecting force, and once into the propellant stream in channel 146, the marking

material travels with the propellant stream out of exit orifice 156 in a direction towards the substrate.

In the event that fusing assistance is required (for example, when an elastic substrate is used, when the marking material particle velocity is low, or the like), a number of approaches can be employed. For example, one or more heated filaments 1122 can be provided proximate the ejection port 156 (shown in FIG. 9), which either reduces the kinetic energy needed to melt the marking material particle or in fact at least partly melts the marking material particle in flight. Alternatively, or in addition to filament 1122, a heated filament 1124 can be located proximate substrate 138 (also shown in FIG. 9) to have a similar effect.

While FIGS. 9 to 13 illustrate a print head 134 having one channel therein, it will be appreciated that a print head according to the present invention can have an arbitrary number of channels, and range from several hundred micrometers across with one or several channels, to a page-width (for example, 8.5 or more inches across) with thousands of channels. The width of each exit orifice 156 can be on the order of 250 μm or smaller, preferably in the range of 100 μm or smaller. The pitch, or spacing from edge to edge (or center to center) between adjacent exit orifices 156 can also be on the order of 250 μm or smaller, preferably in the range of 100 μm or smaller in non-staggered array. In a two-dimensionally staggered array, the pitch can be further reduced.

In some embodiments, the resin is selected so that the resin glass transition temperature is such as to enable kinetic fusing. If the velocity of the toner particles upon impact with the substrate is known, the value of the T_g required to enable kinetic fusing can be calculated as follows:

The critical impact velocity v_c required to melt the toner particle kinetically is estimated for a collision with an infinitely stiff substrate. The kinetic energy E_k of a spherical particle with velocity v , denensity ρ , and diameter d is:

$$E_k = \frac{\pi \cdot \rho \cdot d^3 \cdot v^2}{12}$$

The energy E_m required to heat a spherical particle with diameter d , heat capacity C_p , and density ρ from room temperature T_0 to beyond its glass transition temperature T_g is

$$E_m = \frac{\pi \cdot \rho \cdot d^3 \cdot C_p \cdot (T_g - T_0)}{6}$$

The energy E_p required to deform a particle with diameter d and Young's modulus E beyond its elasticity limit σ_e and into the plastic deformation regime is:

$$E_p = \frac{d^3 \cdot \sigma_e^2}{2E}$$

For kinetic fusing (melting the particle by plastic deformation from the collision with an infinitely stiff substrate), the kinetic energy of the incoming particle should be large enough to bring the particle beyond its elasticity limit. In addition, if the particle is taken beyond its elasticity limit, kinetic energy is transformed into heat through plastic deformation of the particle. If it is assumed that all kinetic energy is transformed into heat, the particle will melt if the kinetic energy (E_k) is larger than the heat required to bring the particle beyond its glass transition temperature (E_m). The critical velocity for obtaining plastic deformation (v_{cp}) can be calculated by equating E_k to E_p :

$$v_{cp} = \sqrt{\frac{6}{\pi \rho E}} \cdot \sigma_e$$

Note that this expression is independent of particle size. Some numerical examples (Source: CRC Handbook) include:

Material	E (Pa)	ρ (kg/m ³)	σ_e (Pa)	v_{cp} (m/s)
Steel	200E9	8,000	700E6	25
Polyethylene	140E6	900	7E6	28
Neoprene	3E6	1,250	20E6	450
Lead	13E9	11,300	14E6	1.6

Most thermoplastic materials (such as polyethylene) require an impact velocity on the order of a few tens of meters per second to achieve plastic deformation from the collision with an infinitely stiff wall. Velocities on the order of several hundred of meters per second are achieved in ballistic aerosol marking processes. The critical velocity for kinetic melt (v_{cm}) can be calculated by equating E_k to E_m :

$$v_{cm} = \sqrt{2 \cdot C_p \cdot (T_s - T_0)}$$

Note that this expression is independent of particle size and density. For example, for a thermoplastic material with $C_p=1000$ J/kg.K and $T_s=60^\circ$ C., $T_0=20^\circ$ C., the critical velocity V_{cm} to achieve kinetic melt is equal to 280 meters per second, which is in the order of magnitude of the ballistic aerosol velocities (typically from about 300 to about 350 meters per second).

In embodiments of the present invention wherein the toner particles of the present invention are used in ballistic aerosol marking processes, the toner particles have average bulk conductivity values typically of no more than about 10 Siemens per centimeter, and preferably no more than about 10^{-7} Siemens per centimeter, and with conductivity values typically no less than about 10^{-11} Siemens per centimeter, although the conductivity values can be outside of these ranges. "Average bulk conductivity" refers to the ability for electrical charge to pass through a pellet of the metal oxide particles having a surface coating of hydrophobic material, measured when the pellet is placed between two electrodes. The particle conductivity can be adjusted by various synthetic parameters of the polymerization; reaction time, molar ratios of oxidant and dopant to pyrrole monomer, temperature, and the like.

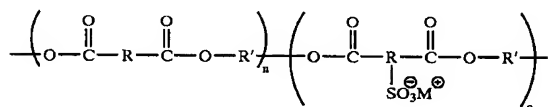
The toners of the present invention comprise particles typically having an average particle diameter of no more than about 13 microns, preferably no more than about 12 microns, more preferably no more than about 10 microns, and even more preferably no more than about 7 microns, although the particle size can be outside of these ranges, and typically have a particle size distribution of GSD equal to no more than about 1.25, preferably no more than about 1.23, and more preferably no more than about 1.20, although the particle size distribution can be outside of these ranges. In some embodiments, larger particles can be preferred even for those toners made by emulsion aggregation processes, such as particles of between about 7 and about 13 microns, because in these instances the toner particle surface area is relatively less with respect to particle mass and accordingly

a lower amount by weight of conductive polymer with respect to toner particle mass can be used to obtain the desired particle conductivity or charging, resulting in a thinner shell of the conductive polymer and thus a reduced effect on the color of the toner. The toner particles comprise a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process.

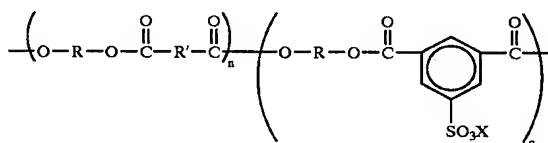
The toners of the present invention comprise particles comprising a polyester resin and an optional colorant. The resin can be a homopolymer of one ester monomer or a copolymer of two or more ester monomers. Examples of suitable resins include polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polypentylene terephthalate, polyhexalene terephthalate, polyheptadene terephthalate, polyoctalene-terephthalate, poly(propylene-diethylene terephthalate), poly(bisphenol A-fumarate), poly(bisphenol A-terephthalate), copoly(bisphenol A-terephthalate-copoly(bisphenol A-fumarate)), poly(neopentyl-terephthalate), sulfonated polyesters such as those disclosed in U.S. Pat. No. 5,348,832, U.S. Pat. No. 5,593,807, U.S. Pat. No. 5,604,076, U.S. Pat. No. 5,648,193, U.S. Pat. No. 5,658,704, U.S. Pat. No. 5,660,965, U.S. Pat. No. 5,840,462, U.S. Pat. No. 5,853,944, U.S. Pat. No. 5,916,725, U.S. Pat. No. 5,919,595, U.S. Pat. No. 5,945,245, U.S. Pat. No. 6,054,240, U.S. Pat. No. 6,017,671, U.S. Pat. No. 6,020,101, application U.S. Ser. No. 08/221,595, now U.S. Pat. No. 6,140,003, application U.S. Ser. No. 09/657,340, now U.S. Pat. No. 6,210,853, application U.S. Ser. No. 09/415,074, now U.S. Pat. No. 6,193,457 and application U.S. Ser. No. 09/624,532, division of application 09/415,074, abandoned, the disclosures of each of which are totally incorporated herein by reference, including salts (such as metal salts, including aluminum salts, salts of alkali metals such as sodium, lithium, and potassium, salts of alkaline earth metals such as beryllium, magnesium, calcium, and barium, metal salts of transition metals, such as scandium, yttrium, titanium, zirconium, hafnium, vanadium, chromium, niobium, tantalum, molybdenum, tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, copper, platinum, silver, gold, zinc, cadmium, mercury, and the like, salts of lanthanide materials, and the like, as well as mixtures thereof) of poly(1,2-propylene-5-sulfoisophthalate), poly(neopentylene-5-sulfoisophthalate), poly(diethylene-5-sulfoisophthalate), copoly(1,2-propylene-5-sulfoisophthalate)-copoly(1,2-propylene-terephthalate phthalate), copoly(1,2-propylene-diethylene-5-sulfoisophthalate)-copoly(1,2-propylene-diethylene-terephthalate phthalate), copoly(ethylene-neopentylene-5-sulfoisophthalate)-copoly(ethylene-neopentylene-terephthalate-phthalate), copoly(propoxylated bisphenol A)-copoly(propoxylated bisphenol A-5-sulfoisophthalate), copoly(ethylene-terephthalate)-copoly(ethylene-5-sulfoisophthalate), copoly(propylene-terephthalate)-copoly(propylene-5-sulfo-isophthalate), copoly(diethylene-terephthalate)-copoly(diethylene-5-sulfo-isophthalate), copoly(propylene-diethylene-terephthalate)-copoly(propylene-diethylene-5-sulfoisophthalate), copoly(propylene-butylene-terephthalate)-copoly(propylene-butylene-5-sulfo-isophthalate), copoly(propoxylated bisphenol-A-fumarate)-copoly(propoxylated bisphenol A-5-sulfo-isophthalate), copoly(ethoxylated bisphenol-A-fumarate)-copoly(ethoxylated bisphenol-A-5-sulfo-isophthalate), copoly(ethoxylated bisphenol-A-maleate)-copoly(ethoxylated bisphenol-A-5-sulfo-isophthalate), copoly(propylene-diethylene terephthalate)-copoly

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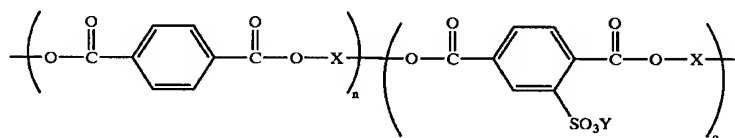
(propylene-5-sulfoisophthalate), copoly(neopentyl-terephthalate)-copoly-(neopentyl-5-sulfoisophthalate), and the like, as well as mixtures thereof. Some examples of suitable polyesters include those of the formula



wherein M is hydrogen, an ammonium ion, or a metal ion, R is an alkylene group, typically with from 1 to about 25 carbon atoms, although the number of carbon atoms can be outside of this range, or an arylene group, typically with from 6 to about 24 carbon atoms, although the number of carbon atoms can be outside of this range, R' is an alkylene group, typically with from 1 to about 25 carbon atoms, although the number of carbon atoms can be outside of this range, or an oxyalkylene group, typically with from 1 to about 20 carbon atoms, although the number of carbon atoms can be outside of this range, n and o each represent the mole percent of monomers, wherein $n+o=100$, and preferably wherein n is from about 92 to about 95.5 and o is from about 0.5 to about 8, although the values of n and o can be outside of these ranges. Also suitable are those of the formula



wherein X is hydrogen, an ammonium ion, or a metal ion, R is an alkylene or oxyalkylene group, typically with from about 2 to about 25 carbon atoms, although the number of carbon atoms can be outside of this range, R' is an arylene or oxyarylene group, typically with from 6 to about 36 carbon atoms, although the number of carbon atoms can be outside of this range, and n and o each represent the numbers of randomly repeating segments. Also suitable are those of the formula



wherein X is a metal ion, X represents an alkyl group derived from a glycol monomer, with examples of suitable glycols including neopentyl glycol, ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, or the like, as well as mixtures thereof, and n and o each represent the numbers of randomly repeating segments. Preferably, the polyester has a weight average molecular weight of from about 2,000 to about 100,000, a number average molecular weight of from about 1,000 to about 50,000, and a polydispersity of from about 2 to about 18 (as measured by gel permeation chromatography), although the

34

weight average and number average molecular weight values and the polydispersity value can be outside of these ranges.

The resin is present in the toner particles in any desired or effective amount, typically at least about 75 percent by weight of the toner particles, and preferably at least about 85 percent by weight of the toner particles, and typically no more than about 99 percent by weight of the toner particles, and preferably no more than about 98 percent by weight of the toner particles, although the amount can be outside of these ranges.

Any desired colorant can be employed. The polypyrrole in or on the toner particles generally imparts a high degree of color to the toner particle, and the toners of the present invention are usually preferred for embodiments wherein black images are desired, but other colorants can also be employed to impart to the toner particles a desired color or tint. Examples of suitable optional colorants include dyes and pigments, such as carbon black (for example, REGAL 3300®), magnetites, phthalocyanines, HELIOGEN BLUE L6900, D6840, D7080, D7020, PYLAM OIL BLUE, PYLAM OIL YELLOW, and PIGMENT BLUE 1, all available from Paul Uhlich & Co., PIGMENT VIOLET 1, PIGMENT RED 48, LEMON CHROME YELLOW DCC 1026, E.D. TOLUIDINE RED, and BON RED C, all available from Dominion Color Co., NOVAPERM YELLOW FGL and HOSTAPERM PINK E, available from Hoechst, CINQUASIA MAGENTA, available from E. I. DuPont de Nemours & Company, 2,9-dimethyl-substituted quinacridone and anthraquinone dyes identified in the Color Index as CI 60710, CI Dispersed Red 15, diazo dyes identified in the Color Index as CI 26050, CI Solvent Red 19, copper tetra (octadecyl sulfonamido) phthalocyanine, x-copper phthalocyanine pigment listed in the Color Index as CI 74160, CI Pigment Blue, Anthrathrene Blue, identified in the Color Index as CI 69810, Special Blue X-2137, diarylide yellow 3,3-dichlorobenzidine acetoacetanilides, a monoazo pigment identified in the Color Index as CI 12700, CI Solvent Yellow 16, a nitrophenyl amine sulfonamide identified in the Color Index as Foron Yellow SE/GLN, CI Dispersed Yellow 33 2,5-dimethoxy-4-sulfonanilide phenylazo-4'-chloro-2,5-dimethoxy acetoacetanilide, Permanent Yellow FGL, Pigment Yellow 74, B 15:3 cyan pigment dispersion, commercially available from Sun Chemicals, Magenta Red 81:3 pigment dispersion, commercially available from Sun

Chemicals, Yellow 180 pigment dispersion, commercially available from Sun Chemicals, colored magnetites, such as mixtures of MAPICO BLACK® and cyan components, and the like, as well as mixtures thereof. Other commercial sources of pigments available as aqueous pigment dispersion from either Sun Chemical or Ciba include (but are not limited to) Pigment Yellow 17, Pigment Yellow 14, Pigment Yellow 93, Pigment Yellow 74, Pigment Violet 23, Pigment Violet 1, Pigment Green 7, Pigment Orange 36, Pigment Orange 21, Pigment Orange 16, Pigment Red 185, Pigment Red 122, Pigment Red 81:3, Pigment Blue 15:3, and Pigment Blue 61, and other pigments that enable reproduction of the maximum Pantone color space. Mixtures of colorants

can also be employed. When present, the optional colorant is present in the toner particles in any desired or effective amount, typically at least about 1 percent by weight of the toner particles, and preferably at least about 2 percent by weight of the toner particles, and typically no more than about 25 percent by weight of the toner particles, and preferably no more than about 15 percent by weight of the toner particles, depending on the desired particle size, although the amount can be outside of these ranges.

The toner particles optionally can also contain charge control additives, such as alkyl pyridinium halides, including cetyl pyridinium chloride and others as disclosed in U.S. Pat. No. 4,298,672, the disclosure of which is totally incorporated herein by reference, sulfates and bisulfates, including distearyl dimethyl ammonium methyl sulfate as disclosed in U.S. Pat. No. 4,560,635, the disclosure of which is totally incorporated herein by reference, and distearyl dimethyl ammonium bisulfate as disclosed in U.S. Pat. No. 4,937,157, U.S. Pat. No. 4,560,635, and copending application Ser. No. 07/396,497, abandoned, the disclosures of each of which are totally incorporated herein by reference, zinc 3,5-di-tert-butyl salicylate compounds, such as Bontron E-84, available from Orient Chemical Company of Japan, or zinc compounds as disclosed in U.S. Pat. No. 4,656,112, the disclosure of which is totally incorporated herein by reference, aluminum 3,5-di-tert-butyl salicylate compounds such as Bontron E-88, available from Orient Chemical Company of Japan, or aluminum compounds as disclosed in U.S. Pat. No. 4,845,003, the disclosure of which is totally incorporated herein by reference, charge control additives as disclosed in U.S. Pat. No. 3,944,493, U.S. Pat. No. 4,007,293, U.S. Pat. No. 4,079,014, U.S. Pat. No. 4,394,430, U.S. Pat. No. 4,464,452, U.S. Pat. No. 4,480,021, and U.S. Pat. No. 4,560,635, the disclosures of each of which are totally incorporated herein by reference, and the like, as well as mixtures thereof. Charge control additives are present in the toner particles in any desired or effective amounts, typically at least about 0.1 percent by weight of the toner particles, and typically no more than about 5 percent by weight of the toner particles, although the amount can be outside of this range.

Examples of optional external surface additives include metal salts, metal salts of fatty acids, colloidal silicas, and the like, as well as mixtures thereof. External additives are present in any desired or effective amount, typically at least about 0.1 percent by weight of the toner particles, and typically no more than about 2 percent by weight of the toner particles, although the amount can be outside of this range, as disclosed in, for example, U.S. Pat. No. 3,590,000, U.S. Pat. No. 3,720,617, U.S. Pat. No. 3,655,374 and U.S. Pat. No. 3,983,045, the disclosures of each of which are totally incorporated herein by reference. Preferred additives include zinc stearate and AEROSIL R812® silica as flow aids, available from Degussa. The external additives can be added during the aggregation process or blended onto the formed particles.

The toner particles of the present invention are prepared by an emulsion aggregation process. This process entails (1) preparing a colorant (such as a pigment) dispersion in a solvent (such as water), which dispersion comprises a colorant, a first ionic surfactant, and an optional charge control agent; (2) shearing the colorant dispersion with a latex mixture comprising (a) a counterionic surfactant with a charge polarity of opposite sign to that of said first ionic surfactant, (b) a nonionic surfactant, and (c) a resin, thereby causing flocculation or heterocoagulation of formed particles of colorant, resin, and optional charge control agent to

form electrostatically bound aggregates, and (3) heating the electrostatically bound aggregates to form stable aggregates of at least about 1 micron in average particle diameter. Toner particle size is typically at least about 1 micron and typically no more than about 7 microns, although the particle size can be outside of this range. Heating can be at a temperature typically of from about 5 to about 50° C. above the resin glass transition temperature, although the temperature can be outside of this range, to coalesce the electrostatically bound aggregates, thereby forming toner particles comprising resin, optional colorant, and optional charge control agent. Alternatively, heating can be first to a temperature below the resin glass transition temperature to form electrostatically bound micron-sized aggregates with a narrow particle size distribution, followed by heating to a temperature above the resin glass transition temperature to provide coalesced micron-sized toner particles comprising resin, optional colorant, and optional charge control agent. The coalesced particles differ from the uncoalesced aggregates primarily in morphology; the uncoalesced particles have greater surface area, typically having a "grape cluster" shape, whereas the coalesced particles are reduced in surface area, typically having a "potato" shape or even a spherical shape. The particle morphology can be controlled by adjusting conditions during the coalescence process, such as pH, temperature, coalescence time, and the like. Optionally, an additional amount of an ionic surfactant (of the same polarity as that of the initial latex) or nonionic surfactant can be added to the mixture prior to heating to minimize subsequent further growth or enlargement of the particles, followed by heating and coalescing the mixture. Subsequently, the toner particles are washed extensively to remove excess water soluble surfactant or surface absorbed surfactant, and are then dried to produce (optionally colored) polymeric toner particles. An alternative process entails using a flocculating or coagulating agent such as poly(aluminum chloride) instead of a counterionic surfactant of opposite polarity to the ionic surfactant in the latex formation; in this process, the growth of the aggregates can be slowed or halted by adjusting the solution to a more basic pH (typically at least about 7 or 8, although the pH can be outside of this range), and, during the coalescence step, the solution can, if desired, be adjusted to a more acidic pH to adjust the particle morphology. The coagulating agent typically is added in an acidic solution (for example, a 1 molar nitric acid solution) to the mixture of ionic latex and dispersed optional colorant, and during this addition step the viscosity of the mixture increases. Thereafter, heat and stirring are applied to induce aggregation and formation of micron-sized particles. When the desired particle size is achieved, this size can be frozen by increasing the pH of the mixture, typically to from about 7 to about 8, although the pH can be outside of this range. Thereafter, the temperature of the mixture can be increased to the desired coalescence temperature, typically from about 80 to about 95° C., although the temperature can be outside of this range. Subsequently, the particle morphology can be adjusted by dropping the pH of the mixture, typically to values of from about 4.5 to about 7, although the pH can be outside of this range.

When particles are prepared without a colorant, the latex (usually around 40 percent solids) is diluted to the right solids loading (of around 12 to 15 percent by weight solids) and then under identical shearing conditions the counterionic surfactant or polyaluminum chloride is added until flocculation or heterocoagulation takes place.

Examples of suitable ionic surfactant include anionic surfactants, such as sodium dodecylsulfate, sodium dode-

cylbenzene sulfonate, sodium dodecylphenylthalesulfate, dialkyl benzenealkyl sulfates and sulfonates, abitic acid, NEOGEN R® and NEOGEN SC® available from Kao, DOWFAX®, available from Dow Chemical Co., and the like, as well as mixtures thereof. Anionic surfactants can be employed in any desired or effective amount, typically at least about 0.01 percent by weight of monomers used to prepare the copolymer resin, and preferably at least about 0.1 percent by weight of monomers used to prepare the copolymer resin, and typically no more than about 10 percent by weight of monomers used to prepare the copolymer resin, and preferably no more than about 5 percent by weight of monomers used to prepare the copolymer resin, although the amount can be outside of these ranges.

Examples of suitable ionic surfactants also include cationic surfactants, such as dialkyl benzenealkyl ammonium chloride, lauryl trimethyl ammonium chloride, alkylbenzyl, methyl ammonium chloride, alkyl benzyl dimethyl ammonium bromide, benzalkonium chloride, cetyl pyridinium bromide, C₁₂, C₁₅, and C₁₇ trimethyl ammonium bromides, halide salts of quaternized polyoxyethylalkylamines, dodecylbenzyl triethyl ammonium chloride, MIRAPOL® and ALKAQUAT® (available from Alkaryl Chemical Company), SANIZOL® (benzalkonium chloride, available from Kao Chemicals), and the like, as well as mixtures thereof. Cationic surfactants can be employed in any desired or effective amounts, typically at least about 0.1 percent by weight of water, and typically no more than about 5 percent by weight of water, although the amount can be outside of this range. Preferably the molar ratio of the cationic surfactant used for flocculation to the anionic surfactant used in latex preparation from about 0.5:1 to about 4:1, and preferably from about 0.5:1 to about 2:1, although the relative amounts can be outside of these ranges.

Examples of suitable nonionic surfactants include polyvinyl alcohol, polyacrylic acid, methalose, methyl cellulose, ethyl cellulose, propyl cellulose, hydroxy ethyl cellulose, carboxy methyl cellulose, polyoxyethylene cetyl ether, polyoxyethylene lauryl ether, polyoxyethylene octyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitan monolaurate, polyoxyethylene stearyl ether, polyoxyethylene nonylphenyl ether, dialkylphenoxypoly(ethyleneoxy) ethanol (available from Rhone-Poulenc as IGEPA CA-2108, IGEPA CA-520®, IGEPA CA-720®, IGEPA CO-890®, IGEPA CO-720®, IGEPA CO-290®, IGEPA CA-210® ANTAROX 890® and ANTAROX 897®), and the like, as well as mixtures thereof. The nonionic surfactant can be present in any desired or effective amount, typically at least about 0.01 percent by weight of monomers used to prepare the copolymer resin, and preferably at least about 0.1 percent by weight of monomers used to prepare the copolymer resin, and typically no more than about 10 percent by weight of monomers used to prepare the copolymer resin, and preferably no more than about 5 percent by weight of monomers used to prepare the copolymer resin, although the amount can be outside of these ranges.

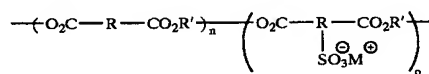
The emulsion aggregation process can entail (1) preparing a colloidal solution comprising a polyester resin and an optional colorant, and (2) adding to the colloidal solution an aqueous solution containing a coalescence agent comprising an ionic metal salt to form toner particles. In embodiments of the present invention wherein the polyester resin is a sulfonated polyester (wherein some of the repeat monomer units of the polymer have sulfonate groups thereon), one preferred emulsion aggregation process comprises admixing a colloidal solution of sulfonated polyester resin with the

colorant, followed by adding to the mixture a coalescence agent comprising an ionic metal salt, and subsequently isolating, filtering, washing, and drying the resulting toner particles. In a specific embodiment, the process comprises (i) mixing a colloidal solution of a sodio-sulfonated polyester resin with a particle size of from about 10 to about 80 nanometers, and preferably from about 10 to about 40 nanometers, and colorant; (ii) adding thereto an aqueous solution containing from about 1 to about 10 percent by weight in water at neutral pH of a coalescence agent comprising an ionic salt of a metal, such as the Group 2 metals (such as beryllium, magnesium, calcium, barium, or the like) or the Group 13 metals (such as aluminum, gallium, indium, or thallium) or the transition metals of Groups 3 to 12 (such as zinc, copper, cadmium, manganese, vanadium, nickel, niobium, chromium, iron, zirconium, scandium, or the like), with examples of suitable anions including halides (fluoride, chloride, bromide, or iodide), acetate, sulfate, or the like; and (iii) isolating and, optionally, washing and/or drying the resulting toner particles. In embodiments wherein uncolored particles are desired, the colorant is omitted from the preparation.

The emulsion aggregation process suitable for making the toner materials for the present invention has been disclosed in previous U.S. patents. For example, U.S. Pat. No. 5,290,654 (Sacripante et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner compositions which comprises dissolving a polymer, and, optionally a pigment, in an organic solvent; dispersing the resulting solution in an aqueous medium containing a surfactant or mixture of surfactants; stirring the mixture with optional heating to remove the organic solvent, thereby obtaining suspended particles of about 0.05 micron to about 2 microns in volume diameter; subsequently homogenizing the resulting suspension with an optional pigment in water and surfactant; followed by aggregating the mixture by heating, thereby providing toner particles with an average particle volume diameter of from between about 3 to about 21 microns when said pigment is present.

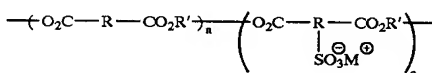
U.S. Pat. No. 5,308,734 (Sacripante et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner compositions which comprises generating an aqueous dispersion of toner fines, ionic surfactant and nonionic surfactant, adding thereto a counterionic surfactant with a polarity opposite to that of said ionic surfactant, homogenizing and stirring said mixture, and heating to provide for coalescence of said toner fine particles.

U.S. Pat. No. 5,348,832 (Sacripante et al.), the disclosure of which is totally incorporated herein by reference, discloses a toner composition comprising pigment and a sulfonated polyester of the formula or as essentially represented by the formula



wherein M is an ion independently selected from the group consisting of hydrogen, ammonium, an alkali metal ion, an alkaline earth metal ion, and a metal ion; R is independently selected from the group consisting of aryl and alkyl; R' is independently selected from the group consisting of alkyl and oxyalkylene; and n and o represent random segments; and wherein the sum of n and o are equal to 100 mole percent. The toner is prepared by an in situ process which

comprises the dispersion of a sulfonated polyester of the formula or as essentially represented by the formula



wherein M is an ion independently selected from the group consisting of hydrogen, ammonium, an alkali metal ion, an alkaline earth metal ion, and a metal ion; R is independently selected from the group consisting of aryl and alkyl; R' is independently selected from the group consisting of alkyl and oxyalkylene; and n and o represent random segments; and wherein the sum of n and o are equal to 100 mole percent, in a vessel containing an aqueous medium of an anionic surfactant and a nonionic surfactant at a temperature of from about 100° C. to about 180° C., thereby obtaining suspended particles of about 0.05 micron to about 2 microns in volume average diameter; subsequently homogenizing the resulting suspension at ambient temperature; followed by aggregating the mixture by adding thereto a mixture of cationic surfactant and pigment particles to effect aggregation of said pigment and sulfonated polyester particles; followed by heating the pigment-sulfonated polyester particle aggregates above the glass transition temperature of the sulfonated polyester causing coalescence of the aggregated particles to provide toner particles with an average particle volume diameter of from between 3 to 21 microns.

U.S. Pat. No. 5,593,807 (Sacripante et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner compositions comprising: (i) preparing an emulsion latex comprising sodio sulfonated polyester resin particles of from about 5 to about 500 nanometers in size diameter by heating said resin in water at a temperature of from about 65° C. to about 90° C.; (ii) preparing a pigment dispersion in a water by dispersing in water from about 10 to about 25 weight percent of sodio sulfonated polyester and from about 1 to about 5 weight percent of pigment; (iii) adding the pigment dispersion to a latex mixture comprising sulfonated polyester resin particles in water with shearing, followed by the addition of an alkali halide in water until aggregation results as indicated by an increase in the latex viscosity of from about 2 centipoise to about 100 centipoise; (iv) heating the resulting mixture at a temperature of from about 45° C. to about 80° C. thereby causing further aggregation and enabling coalescence, resulting in toner particles of from about 4 to about 9 microns in volume average diameter and with a geometric distribution of less than about 1.3; and optionally (v) cooling the product mixture to about 25° C. and followed by washing and drying.

U.S. Pat. No. 5,648,193 (Patel et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner compositions or particles comprising i) flushing a pigment into a sulfonated polyester resin, and which resin has a degree of sulfonation of from between about 2.5 and 20 mol percent; ii) dispersing the resulting sulfonated pigmented polyester resin into water, which water is at a temperature of from about 40 to about 95° C., by a high speed shearing polytron device operating at speeds of from about 100 to about 5,000 revolutions per minute thereby enabling the formation of stable toner sized submicron particles, and which particles are of a volume average diameter of from about 5 to about 200 nanometers; iii) allowing the resulting dispersion to cool to from about 5 to about 10° C. below the glass transition temperature of said pigmented sulfonated polyester resin; iv)

adding an alkali metal halide solution, which solution contains from about 0.5 percent to about 5 percent by weight of water, followed by stirring and heating from about room temperature, about 25° C., to a temperature below the resin Tg to induce aggregation of said submicron pigmented particles to obtain toner size particles of from about 3 to about 10 microns in volume average diameter and with a narrow GSD; or stirring and heating to a temperature below the resin Tg, followed by the addition of alkali metal halide solution until the desired toner size of from about 3 to about 10 microns in volume average diameter and with a narrow GSD is achieved; and v) recovering said toner by filtration and washing with cold water, drying said toner particles by vacuum, and thereafter, optionally blending charge additives and flow additives.

U.S. Pat. No. 5,658,704 (Patel et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner comprising i) flushing pigment into a sulfonated polyester resin, and which resin has a degree of sulfonation of from between about 0.5 and about 2.5 mol percent based on the repeat unit of the polymer; ii) dispersing the resulting pigmented sulfonated polyester resin in warm water, which water is at a temperature of from about 40° to about 95° C., and which dispersing is accomplished by a high speed shearing polytron device operating at speeds of from about 100 to about 5,000 revolutions per minute thereby enabling the formation of toner sized particles, and which particles are of a volume average diameter of from about 3 to about 10 microns with a narrow GSD; iii) recovering said toner by filtration; iv) drying said toner by vacuum; and v) optionally adding to said dry toner charge additives and flow aids.

U.S. Pat. No. 5,660,965 (Mychajlowskij et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner compositions or toner particles comprising generating a latex comprising a sulfonated polyester and olefinic resin in water; generating a pigment mixture comprised of said pigment dispersed in water; shearing said latex and said pigment mixture; adding an alkali (ii) halide; stirring and heating to enable coalescence; followed by filtration and drying.

U.S. Pat. No. 5,840,462 (Foucher et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner which involves i) flushing a colorant into a sulfonated polyester resin; ii) mixing an organic soluble dye with the colorant polyester resin of i); iii) dispersing the resulting mixture into warm water thereby enabling the formation of submicron particles; iv) allowing the resulting solution to cool below about, or about equal to the glass transition temperature of said sulfonated polyester resin; v) adding an alkali halide solution and heating; and optionally vi) recovering said toner, followed by washing and drying.

U.S. Pat. No. 5,853,944 (Foucher et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner with a first aggregation of sulfonated polyester, and thereafter a second aggregation with a colorant dispersion and an alkali halide.

U.S. Pat. No. 5,916,725 (Patel et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner comprising mixing an amine, an emulsion latex containing sulfonated polyester resin, and a colorant dispersion, heating the resulting mixture, and optionally cooling.

U.S. Pat. No. 5,919,595 (Mychajlowskij et al.), the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner comprising

mixing an emulsion latex, a colorant dispersion, and mono-cationic salt, and which mixture possesses an ionic strength of from about 0.001 molar (M) to about 5 molar, and optionally cooling.

U.S. Pat. No. 5,945,245 (Mychajlowski et al.), the disclosure of which is totally incorporated herein by reference, discloses a surfactant free process for the preparation of toner comprising heating a mixture of an emulsion latex, a colorant, and an organic complexing agent.

U.S. Pat. No. 6,054,240 (Julien et al.), the disclosure of which is totally incorporated herein by reference, discloses a yellow toner including a resin, and a colorant comprising a mixture of a yellow pigment and a yellow dye, wherein the combined weight of the colorant is from about 1 to about 50 weight percent of the total weight of the toner, and wherein the chroma of developed toner is from about 90 to about 130 CIELAB units.

U.S. Pat. No. 6,017,671 (Sacripante et al.), the disclosure of which is totally incorporated herein by reference, discloses a toner composition comprising a polyester resin with hydrophobic end groups, colorant, optional wax, optional charge additive, and optional surface additives.

U.S. Pat. No. 6,020,101 (Sacripante et al.), the disclosure of which is totally incorporated herein by reference, discloses a toner comprising a core which comprises a first resin and colorant, and thereover a shell which comprises a second resin and wherein said first resin is an ion complexed sulfonated polyester resin, and said second resin is a transition metal ion complex sulfonated polyester resin.

U.S. Pat. No. 5,604,076 (Patel et al.), the disclosure of which is totally incorporated herein by reference, discloses A process for the preparation of toner compositions comprising: (i) preparing a latex or emulsion resin comprising a polyester core encapsulated within a styrene based resin shell by heating said polyester emulsion containing an anionic surfactant with a mixture of monomers of styrene and acrylic acid, and with potassium persulfate, ammonium persulfate, sodium bisulfite, or mixtures thereof; (ii) adding a pigment dispersion, which dispersion is comprised of a pigment, a cationic surfactant, and optionally a charge control agent, followed by the sharing of the resulting blend; (iii) heating the above sheared blend below about the glass transition temperature (T_g) of the resin to form electrostatically bound toner size aggregates with a narrow particle size distribution; and (iv) heating said electrostatically bound aggregates above about the T_g of the resin.

Application U.S. Ser. No. 09/657,340, filed Sep. 7, 2000 now U.S. Pat. No. 6,210,853, entitled "Toner Aggregation Processes," with the named inventors Raj D. Patel, Michael A. Hopper, Emily L. Moore and Guerino G. Sacripante, the disclosure of which is totally incorporated herein by reference, discloses a process for the preparation of toner including (i) generating by emulsion polymerization in the presence of an initiator a first resin latex emulsion; (ii) generating by polycondensation a second resin latex optionally in the presence of a catalyst; (iib) dispersing the resin of (ii) in water; (iii) mixing (iib) with a colorant thereby providing a colorant dispersion; (iiib) mixing the resin latex emulsion of (i) with the resin/colorant mixture of (iii) to provide a blend of a resin and colorant; (iv) adding an aqueous inorganic cationic coagulant solution of a polymeric metal salt and optionally an organic cationic coagulant to the resin/colorant blend of (iiib); (v) heating at a temperature of from about 5 to about 10 degrees Centigrade below the resin T_g of (i), to thereby form aggregate particles and which particles are optionally at a pH of from about 2 to about 3.5; (vi) adjusting the pH of (v) to about 6.5 to about

9 by the addition of a base; (vii) heating the aggregate particles of (v) at a temperature of from about 5 to about 50 degrees Centigrade above the T_g of the resin of (i), followed by a reduction of the pH to from about 2.5 to about 5 by the addition of an acid resulting in coalesced toner; (viii) optionally isolating the toner.

Application U.S. Ser. No. 09/415,074, filed Oct. 12, 1999 now U.S. Pat. No. 6,143,457, and application U.S. Ser. No. 09/624,532 a division of application 09/415/074, now abandoned, filed Jul. 24, 2000, both entitled "Toner Compositions," with the named inventors Rina Carlini, Guerino G. Sacripante, and Richard P. N. Veregin, the disclosures of each of which are totally incorporated herein by reference, disclose a toner comprising a sulfonated polyester resin, colorant, and thereover a quaternary organic component ionically bound to the toner surface.

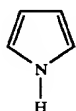
In a particularly preferred embodiment of the present invention (with example amounts provided to indicate relative ratios of materials), the emulsion aggregation process entails first generating a colloidal solution of a sodio-sulfonated polyester resin (about 300 grams in 2 liters of water) by heating the mixture at from about 20 to about 40° C. above the polyester polymer glass transition temperature, thereby forming a colloidal solution of submicron particles in the size range of from about 10 to about 70 nanometers. Subsequently, to this colloidal solution is added a colorant such as Pigment Blue 15:3, available from Sun Chemicals, in an amount of from about 3 to about 5 percent by weight of toner. The resulting mixture is heated to a temperature of from about 50 to about 60° C., followed by adding thereto an aqueous solution of a metal salt such as zinc acetate (5 percent by weight in water) at a rate of from about 1 to about 2 milliliters per minute per 100 grams of polyester resin, causing the coalescence and ionic complexation of sulfonated polyester colloid and colorant to occur until the particle size of the core composite is from about 3 to about 6 microns in diameter (volume average throughout unless otherwise indicated or inferred) with a geometric distribution of from about 1.15 to about 1.25 as measured by the Coulter Counter. Thereafter, the reaction mixture is cooled to about room temperature, followed by filtering, washing once with deionized water, and drying to provide a toner comprising a sulfonated polyester resin and colorant wherein the particle size of the toner is from about 3 to about 6 microns in diameter with a geometric distribution of from about 1.15 to about 1.25 as measured by the Coulter Counter. The washing step can be repeated if desired. The particles are now ready for the conductive polymer surface treatment.

When particles without colorant are desired, the emulsion aggregation process entails diluting with water to 40 weight percent solids the sodio-sulfonated polyester resin instead of adding it to a pigment dispersion, followed by the other steps related hereinabove.

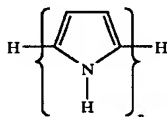
Subsequent to synthesis of the toner particles, the toner particles are washed, preferably with water. Thereafter, polypyrrole is applied to the toner particle surfaces by an oxidative polymerization process. The toner particles are suspended in a solvent in which the toner particles will not dissolve, such as water, methanol, ethanol, butanol, acetone, acetonitrile, blends of water with methanol, ethanol, butanol, acetone, acetonitrile, and/or the like, preferably in an amount of from about 5 to about 20 weight percent toner particles in the solvent, and the pyrrole monomer is added slowly (a typical addition time period would be over about 10 minutes) to the solution with stirring. The monomer typically is added in an amount of from about 5 to about 15

percent by weight of the toner particles. Thereafter, the solution is stirred for a period of time, typically from about 0.5 to about 3 hours. When a dopant is employed, it is typically added at this stage, although it can also be added after addition of the oxidant. Subsequently, the oxidant selected is dissolved in a solvent sufficiently polar to keep the particles from dissolving therein, such as water, methanol, ethanol, butanol, acetone, acetonitrile, or the like, typically in a concentration of from about 0.1 to about 5 molar equivalents of oxidant per molar equivalent of pyrrole monomer, and slowly added dropwise with stirring to the solution containing the toner particles. The amount of oxidant added to the solution typically is in a molar ratio of 1:1 or less with respect to the pyrrole monomer, although a molar excess of oxidant can also be used and can be preferred in some instances. The oxidant is preferably added to the solution subsequent to addition of the pyrrole monomer so that the pyrrole has had time to adsorb onto the toner particle surfaces prior to polymerization, thereby enabling the pyrrole to polymerize on the toner particle surfaces instead of forming separate particles in the solution. When the oxidant addition is complete, the solution is again stirred for a period of time, typically from about 1 to about 2 days, although the time can be outside of this range, to allow the polymerization and doping process to occur. Thereafter, the toner particles having polypyrrole polymerized on the surfaces thereof are washed, preferably with water, to remove therefrom any polymerized pyrrole that formed in the solution as separate particles instead of as a coating on the toner particle surfaces, and the toner particles are dried. The entire process typically takes place at about room temperature (typically from about 15 to about 30° C.), although lower temperatures can also be used if desired.

The polypyrrole is made from pyrrole monomers, of the formula



The polymerized pyrrole (shown in the reduced form) is believed to be of the formula



wherein n is an integer representing the number of repeat monomer units.

Examples of suitable oxidants include water soluble persulfates, such as ammonium persulfate, potassium persulfate, and the like, cerium (IV) sulfate, ammonium cerium (IV) nitrate, ferric salts, such as ferric chloride, iron (III) sulfate, ferric nitrate nanohydrate, tris(p-toluenesulfonato)iron (III) (commercially available from Bayer under the tradename Baytron C), and the like. The oxidant is typically employed in an amount of at least about 0.1 molar equivalent of oxidant per molar equivalent of pyrrole monomer, preferably at least about 0.25 molar equivalent of oxidant per molar equivalent of pyrrole monomer, and more preferably at least about 0.5 molar equivalent of oxidant per molar equivalent of pyrrole monomer, and typically is employed in an amount of no

more than about 5 molar equivalents of oxidant per molar equivalent of pyrrole monomer, preferably no more than about 4 molar equivalents of oxidant per molar equivalent of pyrrole monomer, and more preferably no more than about 3 molar equivalents of oxidant per molar equivalent of pyrrole monomer, although the relative amounts of oxidant and pyrrole can be outside of these ranges.

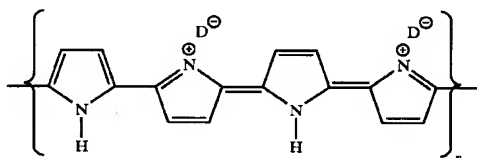
The polarity to which the toner particles prepared by the process of the present invention can be charged can be determined by the choice of oxidant used during the oxidative polymerization of the pyrrole monomer. For example, using oxidants such as ammonium persulfate and potassium persulfate for the oxidative polymerization of the pyrrole monomer tends to result in formation of toner particles that become negatively charged when subjected to triboelectric or inductive charging processes. Using oxidants such as ferric chloride and tris(p-toluenesulfonato)iron (II) for the oxidative polymerization of the pyrrole monomer tends to result in formation of toner particles that become positively charged when subjected to triboelectric or inductive charging processes. Accordingly, toner particles can be obtained with the desired charge polarity without the need to change the toner resin composition, and can be achieved independently of any dopant used with the polypyrrole.

The molecular weight of the polypyrrole formed on the toner particle surfaces need not be high; typically the polymer can have about three or more repeat pyrrole units, and more typically about six or more repeat pyrrole units to enable the desired toner particle conductivity. If desired, however, the molecular weight of the polymer formed on the toner particle surfaces can be adjusted by varying the molar ratio of oxidant to pyrrole monomer, the acidity of the medium, the reaction time of the oxidative polymerization, and/or the like. In specific embodiments, the polymer has at least about 6 repeat 3,4-ethylenedioxythiophene units, and the polymer has no more than about 100 repeat pyrrole units. Molecular weights wherein the number of pyrrole repeat monomer units is about 1,000 or higher can be employed, although higher molecular weights tend to make the material more insoluble and therefore more difficult to process.

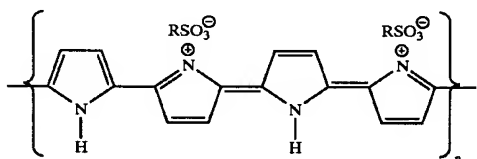
Alternatively, instead of coating the polypyrrole onto the toner particle surfaces, the polypyrrole can be incorporated into the toner particles during the toner preparation process. For example, the polypyrrole can be prepared during the aggregation of the toner latex process to make the toner size particles, and then as the particles coalesced, the polypyrrole can be included within the interior of the toner particles in addition to some polymer remaining on the surface. Another method of incorporating the polypyrrole within the toner particles is to perform the oxidative polymerization of the pyrrole monomer on the aggregated toner particles prior to heating for particle coalescence. As the irregular shaped particles are coalesced with the polypyrrole the pyrrole polymer can be embedded or partially mixed into the toner particles as the particle coalesce. Yet another method of incorporating polypyrrole within the toner particles is to add the pyrrole monomer, dopant, and oxidant after the toner particles are coalesced and cooled but before any washing is performed. The oxidative polymerization can, if desired, be performed in the same reaction kettle to minimize the number of process steps.

When the marking material is used in a process in which the toner particles are triboelectrically charged, the polypyrrole can be in its reduced form. To achieve the desired toner particle conductivity for marking materials suitable for nonmagnetic inductive charging processes or ballistic aerosol marking processes, it is sometimes desirable for the

pyrrole polymer to be in its oxidized form. The pyrrole polymer can be shifted to its oxidized form by doping it with dopants such as sulfonate, phosphate, or phosphonate moieties, iodine, mixtures thereof, or the like. Polypyrrole in its doped and oxidized form is believed to be of the formula



wherein D^- corresponds to the dopant and n is an integer representing the number of repeat monomer units. For example, polypyrrole in its oxidized form and doped with sulfonate moieties is believed to be of the formula



wherein R corresponds to the organic portion of the sulfonate dopant molecule, such as an alkyl group, including linear, branched, saturated, unsaturated, cyclic, and substituted alkyl groups, typically with from 1 to about 20 carbon atoms and preferably with from 1 to about 16 carbon atoms, although the number of carbon atoms can be outside of these ranges, an alkoxy group, including linear, branched, saturated, unsaturated, cyclic, and substituted alkoxy groups, typically with from 1 to about 20 carbon atoms and preferably with from 1 to about 16 carbon atoms, although the number of carbon atoms can be outside of these ranges, an aryl group, including substituted aryl groups, typically with from 6 to about 16 carbon atoms, and preferably with from 6 to about 14 carbon atoms, although the number of carbon atoms can be outside of these ranges, an aryloxy group, including substituted aryloxy groups, typically with from 6 to about 17 carbon atoms, and preferably with from 6 to about 15 carbon atoms, although the number of carbon atoms can be outside of these ranges, an arylalkyl group or an alkylaryl group, including substituted arylalkyl and substituted alkylaryl groups, typically with from 7 to about 20 carbon atoms, and preferably with from 7 to about 16 carbon atoms, although the number of carbon atoms can be outside of these ranges, an arylalkyloxy or an alkylaryloxy group, including substituted arylalkyloxy and substituted alkylaryloxy groups, typically with from 7 to about 21 carbon atoms, and preferably with from 7 to about 17 carbon atoms, although the number of carbon atoms can be outside of these ranges, wherein the substituents on the substituted alkyl, alkoxy, aryl, aryloxy, arylalkyl, alkylaryl, arylalkyloxy, and alkylaryloxy groups can be (but are not limited to) hydroxy groups, halogen atoms, amine groups, imine groups, ammonium groups, cyano groups, pyridine groups, pyridinium groups, ether groups, aldehyde groups, ketone groups, ester groups, amide groups, carbonyl groups, thiocarbonyl groups, sulfate groups, sulfonate groups, sulfide groups, sulfoxide groups, phosphine groups, phosphonium groups, phosphate groups, nitrile groups, mercapto groups, nitro groups, nitroso groups, sulfone groups, acyl groups, acid anhydride groups, azide groups, mixtures thereof, and the

like, as well as mixtures thereof, and wherein two or more substituents can be joined together to form a ring, and n is an integer representing the number of repeat monomer units.

One method of causing the polypyrrole to be doped is to select as the polyester toner resin a sulfonated polyester toner resin. In this embodiment, some of the repeat monomer units in the polyester polymer have sulfonate groups thereon. The sulfonated polyester resin has surface exposed sulfonate groups that serve the dual purpose of anchoring and doping the coating layer of polypyrrole onto the toner particle surface.

Another method of causing the polypyrrole to be doped is to place groups such as sulfonate moieties on the toner particle surfaces during the toner particle synthesis. For example, the ionic surfactant selected for the emulsion aggregation process can be an anionic surfactant having a sulfonate group thereon, such as sodium dodecyl sulfonate, sodium dodecylbenzene sulfonate, dodecylbenzene sulfonic acid, dialkyl benzenealkyl sulfonates, such as 1,3-benzene disulfonic acid sodium salt, para-ethylbenzene sulfonic acid sodium salt, and the like, sodium alkyl naphthalene sulfonates, such as 1,5-naphthalene disulfonic acid sodium salt, 2-naphthalene disulfonic acid, and the like, sodium poly(styrene sulfonate), and the like, as well as mixtures thereof. During the emulsion polymerization process, the surfactant becomes grafted and/or adsorbed onto the latex particles that are later aggregated and coalesced. While the toner particles are washed subsequent to their synthesis to remove surfactant therefrom, some of this surfactant still remains on the particle surfaces, and in sufficient amounts to enable doping of the polypyrrole so that it is desirably conductive.

Yet another method of causing the polypyrrole to be doped is to add small dopant molecules containing sulfonate, phosphate, or phosphonate groups to the toner particle solution before, during, or after the oxidative polymerization of the pyrrole. For example, after the toner particles have been suspended in the solvent and prior to addition of the pyrrole, the dopant can be added to the solution. When the dopant is a solid, it is allowed to dissolve prior to addition of the pyrrole monomer, typically for a period of about 0.5 hour. Alternatively, the dopant can be added after addition of the pyrrole and before addition of the oxidant, or after addition of the oxidant, or at any other time during the process. The dopant is added to the polypyrrole in any desired or effective amount, typically at least about 0.1 molar equivalent of dopant per molar equivalent of pyrrole monomer, preferably at least about 0.25 molar equivalent of dopant per molar equivalent of pyrrole monomer, and more preferably at least about 0.5 molar equivalent of dopant per molar equivalent of pyrrole monomer, and typically no more than about 5 molar equivalents of dopant per molar equivalent of pyrrole monomer, preferably no more than about 4 molar equivalents of dopant per molar equivalent of pyrrole monomer, and more preferably no more than about 3 molar equivalents of dopant per molar equivalent of pyrrole monomer, although the amount can be outside of these ranges.

Examples of suitable dopants include those with *p*-toluene sulfonate anions, such as *p*-toluene sulfonic acid, those with camphor sulfonate anions, such as camphor sulfonic acid, those with dodecyl sulfonate anions, such as dodecane sulfonic acid and sodium dodecyl sulfonate, those with benzene sulfonate anions, such as benzene sulfonic acid, those with naphthalene sulfonate anions, such as naphthalene sulfonic acid, those with dodecylbenzene sulfonate anions, such as dodecylbenzene sulfonic acid and sodium

dodecylbenzene sulfonate, dialkyl benzenealkyl sulfonates, those with 1,3-benzene disulfonate anions, such as 1,3-benzene disulfonic acid sodium salt, those with para-ethylbenzene sulfonate anions, such as para-ethylbenzene sulfonic acid sodium salt, and the like, those with alkyl naphthalene sulfonate anions, such as sodium alkyl naphthalene sulfonates, including those with 1,5-naphthalene disulfonate anions, such as 1,5-naphthalene disulfonic acid sodium salt, and those with 2-naphthalene disulfonate anions, such as 2-naphthalene disulfonic acid, and the like, those with poly(styrene sulfonate) anions, such as poly(styrene sulfonate sodium salt), and the like.

Still another method of doping the polypyrrole is to expose the toner particles that have the polypyrrole on the particle surfaces to iodine vapor in solution, as disclosed in, for example, Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z. H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K.; *Macromolecules*, 1992, 25, 1214 and Yamamoto, T.; Abla, M.; Shimizu, T.; Komarudin, D.; Lee, B.-L.; Kurokawa, E. *Polymer Bulletin*, 1999, 42, 321, the disclosures of each of which are totally incorporated herein by reference.

The polypyrrole thickness on the toner particles is a function of the surface area exposed for surface treatment, which is related to toner particle size and particle morphology, spherical vs potato or raspberry. For smaller particles the weight fraction of pyrrole monomer used based on total mass of particles can be increased to, for example, 20 percent from 10 or 5 percent. The coating weight typically is at least about 5 weight percent of the toner particle mass, and typically is no more than about 20 weight percent of the toner particle mass. Similar amounts are used when the polypyrrole is present throughout the particle instead of as a coating. The solids loading of the washed toner particles can be measured using a heated balance which evaporates off the water, and, based on the initial mass and the mass of the dried material, the solids loading can be calculated. Once the solids loading is determined, the toner slurry is diluted to a 10 percent loading of toner in water. For example, for 20 grams of toner particles the total mass of toner slurry is 200 grams and 2 grams of pyrrole is used. Then the pyrrole and other reagents are added as indicated hereinabove. For a 5 micron toner particle using a 10 weight percent of pyrrole, 2 grams for 20 grams of toner particles the thickness of the conductive polymer shell was 20 nanometers. Depending on the surface morphology, which also can change the surface area, the shell can be thicker or thinner or even incomplete.

The toners of the present invention typically are capable of exhibiting triboelectric surface charging of from about + or -2 to about + or -60 microcoulombs per gram, and preferably of from about + or -10 to about + or -50 microcoulombs per gram, although the triboelectric charging capability can be outside of these ranges. Charging can be accomplished triboelectrically, either against a carrier in a two component development system, or in a single component development system, or inductively.

The marking materials of the present invention can be employed in ballistic aerosol marking processes. Another embodiment of the present invention is directed to a process for depositing marking material onto a substrate which comprises (a) providing a propellant to a head structure, said head structure having at least one channel therein, said channel having an exit orifice with a width no larger than about 250 microns through which the propellant can flow, said propellant flowing through the channel to form thereby a propellant stream having kinetic energy, said channel

directing the propellant stream toward the substrate, and (b) controllably introducing a particulate marking material into the propellant stream in the channel, wherein the kinetic energy of the propellant particle stream causes the particulate marking material to impact the substrate, and wherein the particulate marking material comprises toner particles which comprise a polyester resin, an optional colorant, and polypyrrole, said toner particles having an average particle diameter of no more than about 10 microns and a particle size distribution of GSD equal to no more than about 1.25, wherein said toner particles are prepared by an emulsion aggregation process, said toner particles having an average bulk conductivity of at least about 10^{-11} Siemens per centimeter.

Specific embodiments of the invention will now be described in detail. These examples are intended to be illustrative, and the invention is not limited to the materials, conditions, or process parameters set forth in these embodiments. All parts and percentages are by weight unless otherwise indicated.

The particle flow values of the toner particles were measured with a Hosokawa Micron Powder tester by applying a 1 millimeter vibration for 90 seconds to 2 grams of the toner particles on a set of stacked screens. The top screen contained 150 micron openings, the middle screen contained 75 micron openings, and the bottom screen contained 45 micron openings. The percent cohesion is calculated as follows:

$$\% \text{ cohesion} = 50 \cdot A + 30 \cdot B + 10 \cdot C$$

wherein A is the mass of toner remaining on the 150 micron screen, B is the mass of toner remaining on the 75 micron screen, and C is the mass of toner remaining on the 45 micron screen. (The equation applies a weighting factor proportional to screen size.) This test method is further described in, for example, R. Veregin and R. Bartha, *Proceedings of IS&T 14th International Congress on Advances in Non-Impact Printing Technologies*, pg 358-361, 1998, Toronto, the disclosure of which is totally incorporated herein by reference. For the toners, the input energy applied to the apparatus of 300 millivolts was decreased to 50 millivolts to increase the sensitivity of the test. The lower the percent cohesion value, the better the toner flowability.

Conductivity values of the toners were determined by reparing pellets of each material under 1,000 to 3,000 pounds per square inch and then applying 10 DC volts across the pellet. The value of the current flowing was then recorded, the pellet was removed and its thickness measured, and the bulk conductivity for the pellet was calculated in Siemens per centimeter.

EXAMPLE I

A linear sulfonated random copolyester resin comprising 46.5 mole percent terephthalate, 3.5 mole percent sodium sulfoisophthalate, 47.5 mole percent 1,2-propanediol, and 2.5 mole percent diethylene glycol was prepared as follows. Into a 5 gallon Parr reactor equipped with a bottom drain valve, double turbine agitator, and distillation receiver with a cold water condenser were charged 3.98 kilograms of dimethylterephthalate, 451 grams of sodium dimethyl sulfoisophthalate, 3.104 kilograms of 1,2-propanediol (1 mole excess of glycol), 351 grams of diethylene glycol (1 mole excess of glycol), and 8 grams of butylltin hydroxide oxide catalyst. The reactor was then heated to 165° C. with stirring for 3 hours whereby 1.33 kilograms of distillate were collected in the distillation receiver, and which distillate

comprised about 98 percent by volume methanol and 2 percent by volume 1,2-propanediol as measured by the ABBE refractometer available from American Optical Corporation. The reactor mixture was then heated to 190° C. over a one hour period, after which the pressure was slowly reduced from atmospheric pressure to about 260 Torr over a one hour period, and then reduced to 5 Torr over a two hour period with the collection of approximately 470 grams of distillate in the distillation receiver, and which distillate comprised approximately 97 percent by volume 1,2-propanediol and 3 percent by volume methanol as measured by the ABBE refractometer. The pressure was then further reduced to about 1 Torr over a 30 minute period whereby an additional 530 grams of 1,2-propanediol were collected. The reactor was then purged with nitrogen to atmospheric pressure, and the polymer product discharged through the bottom drain onto a container cooled with dry ice to yield 5.60 kilograms of 3.5 mole percent sulfonated polyester resin, sodio salt of (1,2-propylene-dipropylene-5-sulfoisophthalate)-copoly (1,2-propylene-dipropylene terephthalate). The sulfonated polyester resin glass transition temperature was measured to be 56.6° C. (onset) utilizing the 910 Differential Scanning Calorimeter available from E. I. DuPont operating at a heating rate of 10° C. per minute. The number average molecular weight was measured to be 3,250 grams per mole, and the weight average molecular weight was measured to be 5,290 grams per mole using tetrahydrofuran as the solvent.

A 15 percent by weight solids concentration of the colloidal sulfonated polyester resin dissipated in an aqueous medium was prepared by first heating 2 liters of deionized water to 85° C. with stirring and adding thereto 300 grams of a sulfonated polyester resin, followed by continued heating at about 85° C. and stirring of the mixture for a duration of from about one to about two hours, followed by cooling to room temperature (about 25° C.). The colloidal solution of the sodio-sulfonated polyester resin particles had a characteristic blue tinge and particle sizes in the range of from about 5 to about 150 nanometers, and typically in the range of 20 to 40 nanometers, as measured by a NiCOMP® Particle Size Analyzer.

A 2 liter colloidal solution containing 15 percent by weight of the sodio sulfonated polyester resin was then charged into a 4 liter kettle equipped with a mechanical stirrer. To this solution was added 42 grams of a carbon black pigment dispersion containing 30 percent by weight of REGAL® 330 (available from Cabot, Inc.), and the resulting mixture was heated to 56° C. with stirring at about 180 to 200 revolutions per minute. To this heated mixture was then added dropwise 760 grams of an aqueous solution containing 5 percent by weight of zinc acetate dihydrate. The dropwise addition of the zinc acetate dihydrate solution was accomplished utilizing a peristaltic pump, at a rate of addition of about 2.5 milliliters per minute. After the addition was complete (about 5 hours), the mixture was stirred for an additional 3 hours. A sample (about 1 gram) of the reaction mixture was then retrieved from the kettle, and a particle size of 5.9 microns with a GSD of 1.16 was measured with a Coulter Counter. The mixture was then allowed to cool to room temperature (about 25° C.) overnight (about 18 hours) with stirring. The product was then filtered through a 3 micron hydrophobic membrane cloth and the toner cake was reslurried into about 2 liters of deionized water and stirred for about 1 hour. The toner slurry was refiltered and dried with a freeze drier for 48 hours. The uncoated cyan polyester toner particles with average particle size of 5.9 microns and GSD of 1.16 were pressed into a

pellet and the average bulk conductivity was measured to be $\sigma=1.4 \times 10^{-12}$ Siemens per centimeter.

Into a 250 milliliter glass beaker was placed 75 grams of distilled water along with 6.0 grams of the resultant black polyester toner prepared as described above. This dispersion was then stirred with the aid of a magnetic stirrer to achieve an essentially uniform dispersion of polyester particles in the water. To this dispersion was added 1.01 grams of pyrrole monomer. The pyrrole monomer, with the aid of further stirring, dissolved in under 5 minutes. In a separate 50 milliliter beaker, 10.0 grams of ferric chloride were dissolved in 25 grams of distilled water. Subsequent to the dissolution of the ferric chloride, this solution was added dropwise to the toner in water/pyrrole dispersion. The beaker containing the toner, pyrrole, and ferric chloride was then covered and left overnight under continuous stirring. The toner dispersion was thereafter filtered and the supernatant aqueous solution was measured for conductivity (71 milliSiemens per centimeter). After filtration the toner was washed twice in 600 milliliters of distilled water, filtered, and freeze dried.

The dried product was then submitted for a triboelectric charging measurement. The conductive toner particles were charged by blending 24 grams of carrier particles (65 micron HOEGANES core having a coating in an amount of 1 percent by weight of the carrier, said coating comprising a mixture of poly(methyl methacrylate) and SC Ultra carbon black in a ratio of 80 to 20 by weight) with 1.0 gram of toner particles to produce a developer with a toner concentration (Tc) of 4 weight percent. This mixture was conditioned overnight at 50 percent relative humidity at 22° C., followed by roll milling the developer (toner and carrier) for 30 minutes at 80° F. and 80 percent relative humidity to reach a stable developer charge. The total toner blow off method was used to measure the average charge ratio (QIM) of the developer with a Faraday Cage apparatus (such as described at column 11, lines 5 to 28 of U.S. Pat. No. 3,533,835, the disclosure of which is totally incorporated herein by reference). The conductive particles reached a triboelectric charge of +0.56 microCoulombs per gram. In a separate experiment another 1.0 gram of these toner particles were roll milled for 30 minutes with carrier while at 50° F. and 20 percent relative humidity. In this instance the triboelectric charge reached +1.52 microCoulombs per gram.

The measured average bulk conductivity of a pressed pellet of this toner was 1.1×10^{-2} Siemens per centimeter.

This example demonstrates a positive charging tribo value at both environmental conditions studied (i.e., at 80° F. and 80 percent relative humidity and at 50° F. with 20 percent relative humidity).

EXAMPLE II

Black toner particles were prepared by aggregation of a polyester latex with a carbon black pigment dispersion as described in Example I.

Into a 250 milliliter glass beaker was placed 150 grams of distilled water along with 12.0 grams of the black polyester toner. This dispersion was then stirred with the aid of a magnetic stirrer to achieve an essentially uniform dispersion of polyester particles in the water. To this dispersion was added 2.03 grams of pyrrole monomer. The pyrrole monomer, with the aid of further stirring, dissolved in under 5 minutes. To the solution was then added 2.87 grams of p-toluene sulfonic acid. After dissolution of this acid and 30 minutes of stirring, the pH of the solution was measured to be 1.50 with an Accumet Research AR 20 pH meter. In a

separate 50 milliliter beaker, 17.1 grams of ammonium persulfate were dissolved in 25 grams of distilled water. Subsequent to the dissolution of the ammonium persulfate, this solution was then added dropwise to the toner in water/pyrrole/p-toluene sulfonic acid dispersion. The beaker containing the toner, pyrrole, p-toluene sulfonic acid, and ammonium persulfate was then covered and left overnight under continuous stirring. The toner dispersion was thereafter filtered and the supernatant aqueous solution was measured for conductivity (96 milliSiemens per centimeter). After filtration, the toner was washed twice in 600 milliliters of distilled water, filtered, and freeze dried.

The dried product was then submitted for a triboelectric charging measurement. The conductive toner particles were blended with carrier particles and triboelectric charging was measured as described in Example XX. This mixture was conditioned overnight at 50 percent relative humidity at 22° C., followed by roll milling the developer (toner and carrier) for 30 minutes at 80° F. and 80 percent relative humidity to reach a stable developer charge. The conductive particles reached a triboelectric charge of -3.85 microCoulombs per gram. The triboelectric charge measured for this mixture of toner and carrier roll milled for 30 minutes at 50° F. and 20 percent relative humidity was measured to be -5.86 microCoulombs per gram.

The measured average bulk conductivity of a pressed pellet of this toner was 1.1×10^{-2} Siemens per centimeter.

This example demonstrates a negative charging tribo value.

EXAMPLE III

Additional toners are prepared as described in Examples I and II, varying the relative amount of p-toluene sulfonic acid (mole ratio p-TSA, a ratio of the relative amount of p-TSA by mole percent used with respect to the relative amount by mole percent of pyrrole) and the relative amount of pyrrole (wt. % pyrrole, a measurement of the relative amount of pyrrole by weight used with respect to the relative amount by weight of toner particles). Testing of these toners for Ad conductivity (measured in Siemens per centimeter), tribo charging at 80° F. and 80 percent relative humidity (Q/M A zone, measured in microCoulombs per gram) and at 50° F. and 20 percent relative humidity (Q/M C zone, measured in microCoulombs per gram), and percent cohesion indicated the following:

Toner	mole ratio p-TSA	wt. % pyrrole	Q/M A zone	Q/M C zone	conductivity	% cohesion
1 (control)	0	0	-7.02	-13.49	9.6×10^{-11}	93.8
2	2:1	8.4	-2.58	-3.70	9.0×10^{-5}	94.9
3	1:1	16.8	-3.53	-4.39	9.8×10^{-5}	89.7
4	0.5:1	8.4	-5.76	-5.89	1.8×10^{-5}	96.6
5	1:1	8.4	-4.09	-3.56	1.0×10^{-5}	98.1
6	2:1	16.8	-2.87	-2.58	1.3×10^{-2}	86.4

EXAMPLE IV

Toner compositions are prepared as described in Examples I, II, and III except that no dopant is employed. It is believed that the resulting toner particles will be relatively insulative and suitable for two-component development processes.

EXAMPLE V

Toners are prepared as described in Examples I, II, III, and IV. The toners thus prepared are each admixed with a carrier

as described in Example I to form developer compositions. The developers thus prepared are each incorporated into an electrophotographic imaging apparatus. In each instance, an electrostatic latent image is generated on the photoreceptor and developed with the developer. Thereafter the developed images are transferred to paper substrates and affixed thereto by heat and pressure.

EXAMPLE VI

10 Toners are prepared as described in Examples I to III. The toners are evaluated for nonmagnetic inductive charging by placing each toner on a conductive (aluminum) grounded substrate and touching the toner with a 25 micron thick MYLAR® covered electrode held at a bias of +100 volts. 15 Upon separation of the MYLAR® covered electrode from the toner, it is believed that a monolayer of toner will be adhered to the MYLAR® and that the electrostatic surface potential of the induction charged monolayer will be approximately -100 volts. The fact that the electrostatic surface potential is equal and opposite to the bias applied to the MYLAR® electrode indicates that the toner is sufficiently conducting to enable induction toner charging.

Other embodiments and modifications of the present invention may occur to those of ordinary skill in the art subsequent to a review of the information presented herein; these embodiments and modifications, as well as equivalents thereof, are also included within the scope of this invention.

What is claimed is:

1. A toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein said polypyrrole has at least about 3 repeat monomer units, and wherein said polypyrrole has no more than about 100 repeat monomer units.
2. A toner according to claim 1 wherein the toner particles have an average particle diameter of no more than about 13 microns.
3. A toner according to claim 1 wherein the toner particles comprise a core comprising the polyester resin and optional colorant and, coated on the core, a coating comprising the polypyrrole.
4. A toner according to claim 1 wherein the polyester resin is polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polypentylene terephthalate, polyhexalene terephthalate, polyheptadene terephthalate, polyoctalene-terephthalate, poly(propylene-diethylene terephthalate), poly(bisphenol A-fumarate), poly(bisphenol A-terephthalate), copoly(bisphenol A-terephthalate)-copoly(bisphenol A-fumarate), poly(neopentyl-terephthalate), or mixtures thereof.
5. A toner according to claim 1 wherein the polyester resin is a sulfonated polyester.
6. A toner according to claim 1 wherein the polyester resin is a salt of a poly(1,2-propylene-5-sulfoisophthalate), a poly(neopentylene-sulfoisophthalate), a poly(diethylene-5-sulfoisophthalate), a copoly(1,2-propylene sulfoisophthalate)-copoly-(1,2-propylene-terephthalate phthalate), a copoly(1,2-propylene-diethylene-5-sulfoisophthalate)-copoly-(1,2-propylene-diethylene-terephthalate phthalate), a copoly(ethylene-neopentylene-5-sulfoisophthalate)-copoly-(ethylene-neopentylene-terephthalate-phthalate), a copoly(propoxylated bisphenol A)-copoly-(propoxylated bisphenol A-5-sulfoisophthalate), a copoly(ethylene-terephthalate)-copoly-(ethylene-5-sulfoisophthalate), a copoly(propylene-terephthalate)-copoly-(propylene-5-sulfo-isophthalate), a copoly(diethylene-terephthalate)-copoly-(diethylene-5-sulfo-isophthalate), a

copoly(propylene-diethylene-terephthalate)-copoly(propylene-diethylene-5-sulfoisophthalate), a copoly(propylene-butylene-terephthalate)-copoly(propylene-butylene-5-sulfoisophthalate), a copoly(propoxylated bisphenol-A-fumarate)-copoly(propoxylated bisphenol A-5-sulfo-isophthalate), a copoly(ethoxylated bisphenol-A-fumarate)-copoly(ethoxylated bisphenol-A-5-sulfo-isophthalate), a copoly(ethoxylated bisphenol-A-maleate)-copoly(ethoxylated bisphenol-A-5-sulfo-isophthalate), a copoly(propylene-diethylene terephthalate)-copoly(propylene-5-sulfoisophthalate), a copoly(neopentyl-terephthalate)-copoly(neopentyl-5-sulfoisophthalate), or mixture thereof.

7. A toner according to claim 1 wherein the resin is present in the toner particles in an amount of at least about 75 percent by weight of the toner particles and wherein the resin is present in the toner particles in an amount of no more than about 99 percent by weight of the toner particles.

8. A toner according to claim 1 wherein the toner particles further comprise a pigment colorant.

9. A toner according to claim 1 wherein the toner particles contain a colorant, said colorant being present in an amount of at least about 1 percent by weight of the toner particles, and said colorant being present in an amount of no more than about 25 percent by weight of the toner particles.

10. A toner according to claim 1 wherein the emulsion aggregation process comprises (1) shearing a first ionic surfactant with a latex mixture comprising (a) a counterionic surfactant with a charge polarity of opposite sign to that of said first ionic surfactant, (b) a nonionic surfactant, and (c) a polyester resin, thereby causing flocculation or heterocoagulation of formed particles of resin to form electrostatically bound aggregates; and (2) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter.

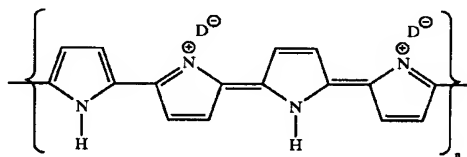
11. A toner according to claim 1 wherein the emulsion aggregation process comprises (1) preparing a colorant dispersion in a solvent, which dispersion comprises a colorant and a first ionic surfactant; (2) shearing the colorant dispersion with a latex mixture comprising (a) a counterionic surfactant with a charge polarity of opposite sign to that of said first ionic surfactant, (b) a nonionic surfactant, and (c) a polyester resin, thereby causing flocculation or heterocoagulation of formed particles of colorant and resin to form electrostatically bound aggregates; and (3) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter.

12. A toner according to claim 1 wherein the emulsion aggregation process comprises (1) shearing an ionic surfactant with a latex mixture comprising (a) a flocculating agent, (b) a nonionic surfactant, and (c) a polyester resin, thereby causing flocculation or heterocoagulation of formed particles of colorant and resin to form electrostatically bound aggregates; and (2) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter.

13. A toner according to claim 1 wherein the emulsion aggregation process comprises (1) preparing a colorant dispersion in a solvent, which dispersion comprises a colorant and an ionic surfactant; (2) shearing the colorant dispersion with a latex mixture comprising (a) a flocculating agent, (b) a nonionic surfactant, and (c) a polyester resin, thereby causing flocculation or heterocoagulation of formed particles of colorant and resin to form electrostatically bound aggregates; and (3) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter.

14. A toner according to claim 1 wherein the emulsion aggregation process comprises (1) preparing a colloidal solution comprising a polyester resin and an optional colorant, and (2) adding to the colloidal solution an aqueous solution containing a coalescence agent comprising an ionic metal salt to form toner particles.

15. A toner according to claim 1 wherein the polypyrrole is of the formula



wherein D⁻ corresponds to the dopant and n is an integer representing the number of repeat monomer units.

16. A toner according to claim 1 wherein the polypyrrole is doped with iodine, molecules containing sulfonate groups, molecules containing phosphate groups, molecules containing phosphonate groups, or mixtures thereof.

17. A toner according to claim 1 wherein the polypyrrole is doped with sulfonate containing anions of the formula RSO₃⁻ wherein R is an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an arylalkyl group, an alkylaryl group, an arylalkyloxy group, an alkylaryloxy group, or mixtures thereof.

18. A toner according to claim 1 wherein the polypyrrole is doped with anions selected from p-toluene sulfonate, camphor sulfonate, benzene sulfonate, naphthalene sulfonate, dodecyl sulfonate, dodecylbenzene sulfonate, dialkyl benzenealkyl sulfonates, para-ethylbenzene sulfonate, alkyl naphthalene sulfonates, poly(styrene sulfonate), or mixtures thereof.

19. A toner according to claim 1 wherein the polypyrrole is doped with anions selected from p-toluene sulfonate, camphor sulfonate, benzene sulfonate, naphthalene sulfonate, dodecyl sulfonate, dodecylbenzene sulfonate, 1,3-benzene disulfonate, para-ethylbenzene sulfonate, 1,5-naphthalene disulfonate, 2-naphthalene disulfonate, poly(styrene sulfonate), or mixtures thereof.

20. A toner according to claim 1 wherein the polypyrrole is doped with a dopant present in an amount of at least about 0.1 molar equivalent of dopant per molar equivalent of pyrrole monomer and present in an amount of no more than about 5 molar equivalents of dopant per molar equivalent of pyrrole monomer.

21. A toner according to claim 1 wherein the polypyrrole is doped with a dopant present in an amount of at least about 0.25 molar equivalent of dopant per molar equivalent of pyrrole monomer and present in an amount of no more than about 4 molar equivalents of dopant per molar equivalent of pyrrole monomer.

22. A toner according to claim 1 wherein the polypyrrole is doped with a dopant present in an amount of at least about 0.5 molar equivalent of dopant per molar equivalent of pyrrole monomer and present in an amount of no more than about 3 molar equivalents of dopant per molar equivalent of pyrrole monomer.

23. A toner according to claim 1 wherein the toner particles have an average bulk conductivity of no more than about 10⁻¹² Siemens per centimeter.

24. A toner according to claim 1 wherein the toner particles have an average bulk conductivity of no more than about 10⁻¹³ Siemens per centimeter, and wherein the toner

particles have an average bulk conductivity of no less than about 10^{-16} Siemens per centimeter.

25. A toner according to claim 1 wherein the toner particles have an average bulk conductivity of no less than about 10^{-11} Siemens per centimeter.

26. A toner according to claim 1 wherein the toner particles have an average bulk conductivity of no less than about 10^{-7} Siemens per centimeter, and wherein the toner particles have an average bulk conductivity of no more than about 10 Siemens per centimeter.

27. A toner according to claim 1 wherein the toner particles have an average bulk conductivity of no more than about 10 Siemens per centimeter.

28. A toner according to claim 1 wherein the toner particles have an average bulk conductivity of no more than about 10^{-7} Siemens per centimeter.

29. A toner according to claim 1 wherein the polypyrrole is present in an amount of at least about 5 weight percent of the toner particle mass and wherein the polypyrrole is present in an amount of no more than about 20 weight percent of the toner particle mass.

30. A toner according to claim 1 wherein said toner particles are nonmagnetic.

31. A toner according to claim 1 wherein the polypyrrole has at least about 6 repeat monomer units and wherein the polypyrrole has no more than about 100 repeat monomer units.

32. A toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein the toner particles comprise a core comprising the polyester resin and optional colorant, said core having a surface, and, coated on the core, a coating comprising the polypyrrole, wherein the polyester resin is a sulfonated polyester resin, and wherein the sulfonated polyester resin anchors the polypyrrole to the core surface.

33. A toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein the toner particles comprise a core comprising the polyester resin and optional colorant and, coated on the core, a coating comprising the polypyrrole, wherein the polyester resin is a sulfonated polyester, and wherein the sulfonated polyester resin acts as a dopant for the polypyrrole.

34. A toner according to claim 33 wherein the polyester resin is a poly(1,2-propylene-5-sulfoisophthalate), a poly(neopentylene-5-sulfoisophthalate), a poly(diethylene-5-sulfoisophthalate), a copoly(1,2-propylene-5-sulfoisophthalate)-copoly-(1,2-propylene-terephthalate phthalate), a copoly(1,2-propylene-diethylene-5-sulfoisophthalate)copoly-(1,2-propylene-diethylene-terephthalate phthalate), a copoly(ethylene-neopentylene-5-sulfoisophthalate)copoly-(ethylene-neopentylene-terephthalate-phthalate), a copoly(propoxylated bisphenol A)copoly-(propoxylated bisphenol A-5-sulfoisophthalate), a copoly(ethylene-terephthalate)-copoly-(ethylene-5-sulfoisophthalate), a copoly(propylene-terephthalate)-copoly-(propylene-5-sulfoisophthalate), a copoly(diethylene-terephthalate)-copoly-(diethylene-5-sulfoisophthalate), a copoly(propylene-diethylene-terephthalate)-copoly-(propylene-diethylene-5-sulfoisophthalate), a copoly(propylene-butylene-terephthalate)-copoly(propylene-butylene-5-sulfoisophthalate), a copoly(propoxylated bisphenol-A-fumarate)-copoly(propoxylated bisphenol A-5-sulfoisophthalate), a copoly(ethoxylated bisphenol-A-fumarate)-copoly(ethoxylated bisphenol-A-5-sulfoisophthalate), a copoly(ethoxylated bisphenol-A-maleate)-

copoly(ethoxylated bisphenol-A-5-sulfoisophthalate), a copoly(propylene-diethylene terephthalate)-copoly(propylene-5-sulfoisophthalate), a copoly(neopentyl-terephthalate)-copoly-(neopentyl-&sulfoisophthalate), or a mixture thereof.

35. A toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein the emulsion aggregation process comprises (1) shearing a first ionic surfactant with a latex mixture comprises (a) a counterionic surfactant with a charge polarity of opposite sign to that of said first ionic surfactant, (b) a nonionic surfactant and (c) the polyester resin, thereby causing flocculation or heterocoagulation of formed particles of resin to form electrostatically bound aggregates; and (2) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter, wherein the toner particles comprise a core comprising the polyester resin and optional colorant, said core having a surface, and, coated on the core, a coating comprising the polypyrrole, wherein the ionic surfactant has a sulfonate group thereon, wherein the ionic surfactant remains on the core surface, and wherein the ionic surfactant acts as a dopant for the polypyrrole.

36. A toner comprising particles of a polyester resin, a colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein the emulsion aggregation process comprises (1) preparing a colorant dispersion in a solvent, which dispersion comprises the colorant and a first ionic surfactant; (2) shearing the colorant dispersion with a latex mixture comprising (a) a counterionic surfactant with a charge polarity of opposite sign to that of said first ionic surfactant, (b) a nonionic surfactant, and (c) the polyester resin, thereby causing flocculation or heterocoagulation of formed particles of colorant and resin to form electrostatically bound aggregates; and (3) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter, wherein the toner particles comprise a core comprising the polyester resin and colorant, said core having a surface, and, coated on the core, a coating comprising the polypyrrole, wherein the ionic surfactant has a sulfonate group thereon, wherein the ionic surfactant remains on the core surface, and wherein the ionic surfactant acts as a dopant for the polypyrrole.

37. A toner comprising particles of a polyester resin, an optional colorant, and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein the emulsion aggregation process comprises (1) shearing an ionic surfactant with a latex mixture comprising (a) a flocculating agent, (b) a nonionic surfactant, and (c) the polyester resin, thereby causing flocculation or heterocoagulation of formed particles of resin to form electrostatically bound aggregates; and (2) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter, wherein the toner particles comprise a core comprising the polyester resin and optional colorant, said core having a surface, and, coated on the core, a coating comprising the polypyrrole, wherein the ionic surfactant has a sulfonate group thereon, wherein the ionic surfactant remains on the core surface, and wherein the ionic surfactant acts as a dopant for the polypyrrole.

38. A toner comprising particles of a polyester resin, a colorant and polypyrrole, wherein said toner particles are prepared by an emulsion aggregation process, wherein the emulsion aggregation process comprises (1) preparing a colorant dispersion in a solvent, which dispersion comprises

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the colorant and an ionic surfactant; (2) shearing the colorant dispersion with a latex mixture comprising (a) a flocculating agent, (b) a nonionic surfactant, and (c) the polyester resin, thereby causing flocculation or heterocoagulation of formed particles of colorant and resin to form electrostatically bound aggregates; and (3) heating the electrostatically bound aggregates to form aggregates of at least about 1 micron in average particle diameter, wherein the toner

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particles comprise a core comprising the polyester resin and colorant, said core having a surface, and, coated on the core, a coating comprising the polypyrrole, wherein the ionic surfactant has a sulfonate group thereon, wherein the ionic surfactant remains on the core surface, and wherein the ionic surfactant acts as a dopant for the polypyrrole.

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US006150062A

United States Patent [19]**Sugizaki et al.**[11] **Patent Number:** **6,150,062**[45] **Date of Patent:** **Nov. 21, 2000**

[54] **TONERS FOR DEVELOPING
ELECTROSTATIC LATENT IMAGES,
DEVELOPERS FOR ELECTROSTATIC
LATENT IMAGES AND METHODS FOR
FORMING IMAGES**

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[52] U.S. Cl. **430/45; 430/110; 430/111;
430/126**

[58] Field of Search **430/45, 110, 111,
430/126**

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[57] **ABSTRACT**

A toner for developing an electrostatic latent image includes at least coloring particles containing a colorant and a binder resin. The volume average particle size of the coloring particle is 1.0 to 5.0 μm . The toner is further characterized in that (1) the relationship between the quantity of the electric charge and the particle size is adjusted appropriately, (2) the particle size distribution is adjusted appropriately and/or (3) an external additive comprising at least an ultra microparticle and a super-ultra microparticle may be added, the rate of coating on the coloring particle being adjusted appropriately. A method for forming an image includes (1) a developing step in which a toner layer is formed on the surface of a developer support arranged opposed to a latent image support and an electrostatic latent image on the latent image support is developed with the toner layer to obtain a toner image and (2) a transfer step in which the toner image formed is transferred to a transfer material. The Rz of at least an image receiving region of the transfer material provided for the transfer step is preferably 10 μm or less.

37 Claims, 1 Drawing Sheet

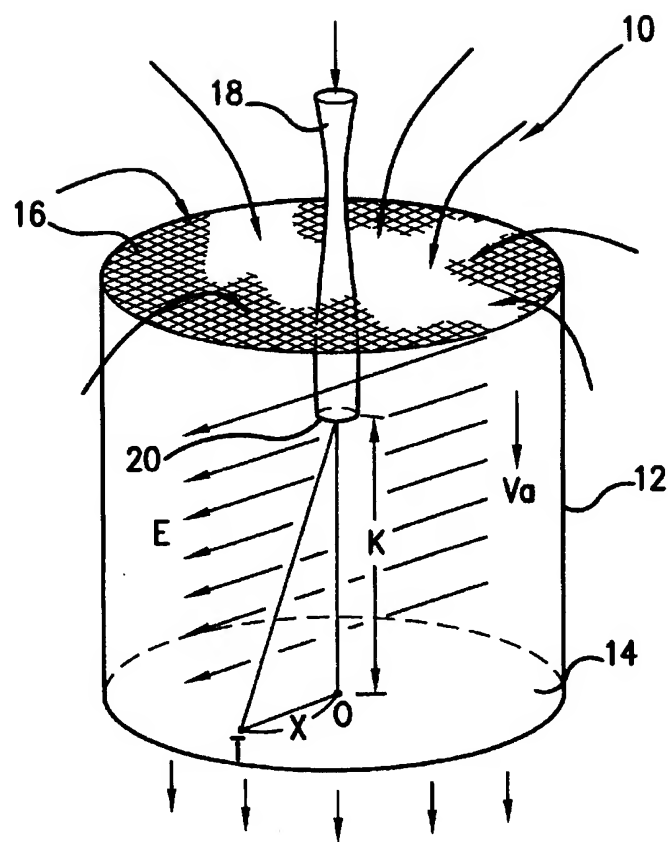


FIG. 1

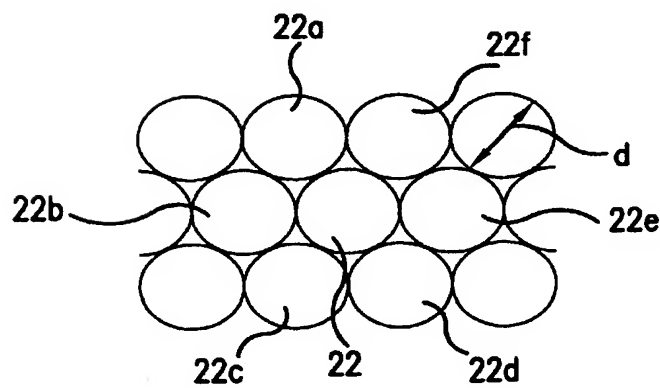


FIG. 2

TONERS FOR DEVELOPING ELECTROSTATIC LATENT IMAGES, DEVELOPERS FOR ELECTROSTATIC LATENT IMAGES AND METHODS FOR FORMING IMAGES

BACKGROUND OF THE INVENTION

1. Field of Invention

The present invention relates to toners for developing an electrostatic latent image, developers for an electrostatic latent image and methods for forming an image employed in electrophotography, electrostatic recording, electrostatic printing and the like. More particularly, the present invention relates to toners for developing an electrostatic latent image, developers for an electrostatic latent image and methods for forming an image using the same for the purpose of developing a digital electrostatic latent image.

2. Description of Related Art

In electrophotography, a toner contained in a developer is deposited onto a latent image formed on a photoconductor and then transferred onto a transfer material such as paper or a plastic film. The toner is then fixed by, for example, heating to form an image. The developer used in this process includes a two-component developer comprising a toner and a carrier and a one-component developer such as a magnetic toner. A two-component developer is widely employed because of its preferable controllability due to the fact that the functions of the developer, such as agitation, transportation and electric charging, are shared with a carrier.

On the other hand, increasing numbers of printers and copiers employing electrophotography have, for the past several years, come to involve a color toning technology and achieved finer electrostatic latent images in response to a higher resolution achieved by improved devices. As a result, accurate development of a latent image and a higher quality of an image have been sought to be obtained by reducing the particle size of a toner. Especially in a full color copier by which a digital image is developed, transferred and fixed using color toners, the quality of an image is increased to some extent by using a small-sized toner having a particle size as small as 7 to 8 μm .

Nevertheless, a further smaller particle size and a more accurate particle size distribution will be required to respond to the recent demand for a higher resolution (improved reproducibility of minute lines, improved gradation, etc.). Reduction in the particle size of a toner is accompanied with increased non-static adhesive forces such as van der Waals force, resulting in an increased cohesive force between toner particles which may lead to a markedly poor particulate flowability or resulting in an increased adhesive force of a toner onto a carrier or a photoconductor surface which may lead to poorer developing and transfer performances, thus causing a reduced image density, which is accompanied occasionally with a marked reduction in ability of cleaning the residual toner on the surface of the photoconductor.

In addition, a reduced charge exchange between the toner and the carrier as a result of a reduced particle performance associated with the reduction in the toner particle size may cause a retarded charging, resulting in a broader charge distribution, which may lead to defects of the image such as fogging. Moreover, the reduction in the particle size of a toner causes a reduced charging performance at a high temperature and a high humidity as well as an evidently retarded charging at a low temperature and a low humidity.

A small-sized toner for full color printing gives a thinner toner layer on a transfer material, thereby requiring a higher

concentration of the colorant in the toner. In this case, the charging performance of the colorant contained in the toner is affected more evidently, resulting in a disadvantageously greater difference in electric charge quantity, charging speed, temperature and humidity dependence of the charging between full color toners such as cyan, magenta, yellow and black. This constitutes a considerable problem to be solved. Because of this problem, the formation of a high quality image using a toner having a particle size as small as 6 μm or less has not been established practically.

The thickness of an image formed on a transfer material such as transfer paper (hereinafter referred simply to as "image thickness") is several μm or less in offset printing, but is as large as 10 μm to 20 μm in an electrophotographic process. This is so even when the particle sizes of the toners are as small as 7 to 8 μm because of, for example, the need to form at least three toner layers in the case of the process using full color toners. An image having such a large image thickness tends to exhibit an unusual visual impression. Accordingly, in order to achieve an image of a quality as high as that obtained by transfer printing, it is required to eliminate the difference in the image structure from the transfer printing, i.e., to reduce the image thickness. The image thus formed by mounting a large amount of the toners on the transfer material as described above is readily damaged due to its uneven and irregular surface, resulting in a poor durability of the image once formed.

Accordingly, various attempts have been made to improve full color toners. For example, Japanese Patent Application Laid-Open No. 6-75430, No. 6-332237, No. 7-77824, No. 7-77825 and No. 7-146589 propose a use of a toner whose weight average particle size is 3 to 7 μm , and in which a toner having a particle size of 5.04 μm or less is contained in an amount of 40% by number or more, a toner having a particle size of 4 μm or less is contained in an amount of 20 to 70% by number, a toner having a particle size of 8 μm or more is contained in an amount of 2 to 20% by number and a toner having a particle size of 10.8 μm or more is contained in an amount of 6% by number or less, for the purpose of obtaining an image having a high image density as well as excellent highlight reproducibility and minute line reproducibility.

Japanese Patent Application Laid-Open No. 7-146589 proposes the use of a toner whose weight average particle size is 3.5 to 7.5 μm , and in which a toner having a particle size of 5.04 μm or less is contained in an amount of 35% by number or more, a toner having a particle size of 4 μm or less is contained in an amount of 15% by number or more, a toner having a particle size of 8 μm or more is contained in an amount of 2 to 20% by number and a toner having a particle size of 10.8 μm or more is contained in an amount of 6% by number or less, for the purpose of obtaining an image having a high image density as well as excellent highlight reproducibility and minute line reproducibility.

A small-sized toner discussed in the references listed above has a weight average particle size of the toner particles ranging from 3 to 7 μm , but does not contain toner particles having a size of 5 μm or less in sufficiently large amounts. This allows only a limited improvement in the image quality to be achieved with such a toner. Thus, if such toners are used, there are limits to the improvement in the image quality regarding minute line reproducibility and gradation. Moreover, no discussion is made with regard to the relationship between the amount of the toner having a particle size of 1 μm or less and the characteristics of the toner.

Japanese Patent Application Laid-Open No. 8-227171 proposes a method for imparting excellent transferability

and cleanability and for ameliorating the deterioration of toner characteristics due to deterioration of an additive, by means of adding to a toner having a certain form coefficient and a weight average particle size of 1 to 9 μm , a 10 to 90 nm sized inorganic powder and a 30 to 120 nm sized silicon compound microparticle imparted with hydrophobicity.

However, since this toner is combined with an additive having a broad particle size distribution and is not discussed with regard to the rate of the coating onto the toner particle, it cannot be imparted with appropriate particle flowability, particle adhesion ability and electric charging ability when formulated into a toner having a volume average particle size of 5 μm or less, and thus cannot achieve an improved image quality attributable to a small-sized toner. In fact, the weight average particle size of the toner particle described in the examples of this reference is at least 6 μm .

It has also been known to produce toners comprised of polymeric particles impregnated with a dye produced by dispersion polymerization. In this method, the polymeric particle size is perfectly controlled so that all of the particles are of the same size, i.e., there is no particle size distribution. However, this method is used with dyes as colorants and not pigments.

Reduction in the toner size may also lead to difficulty in preserving the electric charge quantity of the toner required for development and in some cases may result in a counter-polarly charged toner. An insufficiently charged toner or a counter-polarly charged toner may cause a blank area in the image or may allow fogging in a non-image region to occur easily. When the electric charge quantity is excessive, the electrostatic adhesion ability becomes too high, resulting in a reduced density or an uneven image structure. Thus, since a smaller-sized toner allows the charging state of an individual toner particle to have a higher effect on the resulting image, it is very important to ensure an appropriate frequency distribution of the electric charge quantity. However, the toners proposed in the references listed above do not discuss the frequency distribution of the electric charge quantity, and practically tend to result in a toner having an insufficient charge, a counter-polarly charged toner and an excessively charged toner, and also still involve the problems of image deterioration such as fogging in a non-image region, a reduced density and an uneven image.

On the other hand, a wet electrophotographic method has been used to avoid the poor qualitative impression of an image by a dry electrophotographic method as described above. The wet electrophotographic method is a procedure in which an image is obtained by developing the image with a liquid developer formed by dispersing a microparticulate toner having an average size of 1 to 2 μm in a carrier fluid such as a petroleum-based solvent having a high boiling point. The method is useful to improve the minute line reproducibility, to reduce the disturbance of the image on a transfer material and to reduce the thickness of an image, thus providing a higher image quality.

Nevertheless, the wet electrophotographic method also involves disadvantages such as reduction in the image quality due to the smeared image, i.e., a toner image on the photoconductor can be distorted by the carrier fluid upon formation of the image forming on the photoconductor. In addition, the method requires a large-sized device which is not suitable for an ordinary office or domestic use, since it must be fitted with a solvent recovery system to avoid the release of the solvents such as the petroleum-based organic solvent having a high boiling point to escape from the instrument. It is undesirable also in view of environmental pollution.

Accordingly, a toner for developing an electrostatic latent image which is applicable to a dry electrophotographic method and which is excellent in terms of minute line reproducibility and stability against environment is sought.

While the problems associated with a conventional small-sized toner are discussed above in connection with the formation of a full color image, a smaller-sized toner is desirable also in the case where an image is obtained in a monochrome system, especially when using only a black toner, since the improved minute line reproducibility and the improved gradation are required similarly and the smaller size of the toner is attributable to improve the image quality also in view of the image thickness.

Also, as a factor for determining the image quality of an image obtained, the surface state of a transfer material appears to be extremely important.

When an ordinary non-coat paper, a high quality paper or copy paper for monochrome printing, etc., is used as a transfer material, there may be a problem that the surface smoothness is insufficient. Moreover, the coloring ability may be decreased as adversely affected by fibers of the adjacent paper when toner particles locate in concave parts of the surface of the paper. Also, the color mixing ability may be deteriorated in the case of secondary colors or tertiary colors. As to the minute line reproducibility, scattering of the thickness may more readily occur and may not be sufficient. In addition, when the toner is not located in the concave parts but instead covers the concave parts but leaves a space in the concave parts, there is an inadequate foundation and thus the toner is not fixed during fixing, and the problem of offset to the fixing roll may occur. In particular, when a small-sized toner is used, the above problems caused by the roughness of the surface state may more easily occur.

When a material having a high surface smoothness such as coat paper is used as a transfer material, since uniform heat and pressure are provided to the toner at fixing, a uniform image having a high glossiness can be obtained. However, if a toner weight per unit area of the toner image on a transfer material is too high, a problem such as spread out of an image at fixing, and a problem such that a glaring image having an excessively high glossiness is obtained and the visual uniformity is decreased, may occur.

In addition, when a material having a paper uniformity and minute unevenness such as mat coat paper, etc. is used as a transfer material, since a toner is fixed to follow the minute unevenness on the surface, the increase of glossiness may be restrained and a uniform image having a low glossiness may be obtained. However, if the toner weight of toner image on a transfer material is too high, the toner existing on the convex is largely molten and glossiness may be increased so that the difference with the glossiness of the transfer material may be increased and the uniformity of image glossiness may be decreased.

As described, there is a problem such that a satisfactory image may not be obtained when a smoothness of the surface of a transfer material is not sufficient. Also, if a toner weight of the toner image on a transfer material is too high, an image having a high uniformity may not be obtained even when the smoothness is high to some extent or sufficiently high.

As a proposal to obtain a high image quality of an image in relation to the surface state of a transfer material and a toner, there is an image forming method by electrostatic copying described in Japanese Patent Application Laid-Open No. 63-123056. In this reference, an image forming method is described in which a toner image developed from

an electrostatic latent image using a toner particle which has average radius (avg) of about $5\text{ }\mu\text{m}$ or less, 90% of the entire of which is in the range from about $(0.8 \times \text{avg})\text{ }\mu\text{m}$ to about $(1.2 \times \text{avg})\text{ }\mu\text{m}$ and 99% of the entire of which is in the range from about $(0.5 \times \text{avg})\text{ }\mu\text{m}$ to about $(2 \times \text{avg})\text{ }\mu\text{m}$, is transferred electrostatically to the surface of a receiver layer, the surface of which has a peak highness of about $(0.3 \times \text{avg})\text{ }\mu\text{m}$ or less. Although it is described that the toner particle may have a size within the range of 1 to $10\text{ }\mu\text{m}$, it is not indicated whether or not this is on a number average basis or volume average basis. Moreover, in an example in the reference, a dye is used as the colorant instead of a pigment.

With the method, it is described that a low graininess and a high resolution can be attained by corresponding the surface of a transfer material and a profile of the particle size distribution of a toner particle in order to make the adhesive force between the latent image support and toner particles and the adhesive force between the transfer material and toner particles the same, and then applying an electrostatic force in this state to fix.

However, this prior art method cannot be applied to a full-color image formation process requiring a plurality of transfers of toners having different color phases to a transfer material. In addition, in relation with the toner particles to be transferred, the image obtained is largely affected by the surface state of the transfer material, and thus the transfer material to be selected is extremely limited.

Japanese Patent Applications Laid-Open Nos. 5-6033 and Nos. 5-127437 propose a process in which contrarotate developing is made on a non-image region, a transparent toner layer is subsequently formed thereon, a uniform toner layer is formed over the entire of an image region and a non-image region, and the whole of the transfer material surface is smoothed to produce a high gloss image.

However, with the method, the transparent toner amount on the non-image region is 1 to 8 mg/cm^2 , compared with the color toner amount on the image region of 0.5 to 5 mg/cm^2 . Also, the whole of the transfer material surface is covered by the thick toner layer and thus the transfer material is largely curled. In addition, when the large amount of toner layer is formed on the entire of the non-image region, there is a problem that the consumption amounts of both the color toner and the transparent toner are increased largely, and the cost is thus increased. Further, in these image forming methods, no discussion on the particle size and particle size distribution of toner is made, and thus with the method, the minute line reproducibility and gradation cannot be improved and the image quality obtained is not satisfactory.

SUMMARY OF THE INVENTION

An objective of the present invention is to provide a toner for developing an electrostatic latent image, which allows excellent minute line reproducibility and excellent gradation and is capable of forming an image without fogging and which has a high transfer efficiency and an excellent durability, a developer incorporating such toner for developing an electrostatic latent image, as well as a method for forming an image employing the same. More particularly, it is an objective to provide a toner for developing an electrostatic latent image, a developer for an electrostatic latent image and a method for forming an image, especially for developing a digital electrostatic latent image.

A further objective of the present invention is to provide a toner for developing an electrostatic latent image, a

developer for an electrostatic latent image and a method for forming an image, which is capable of providing an image of a quality which is equal to or higher than an image obtained by offset printing.

A still further objective of the present invention is to provide a toner for developing an electrostatic latent image whose charging characteristics are not subjected to the effects of temperature and humidity, which is readily charged (i.e., which is "stable satisfactorily to environment", on the contrary to "dependent on environment" referred to in case of dependency on the environmental factors) and which maintains a sharp charge distribution even when the toner is newly added into the developing unit.

A still further objective of the present invention is to provide a method for forming an image, which allows an excellent minute line reproducibility and excellent gradation, which is capable of providing a uniform image glossiness corresponding to the surface glossiness of a transfer material itself, and which is capable of providing an image quality which is equal to or higher than an image obtained by an offset printing, with a small-sized toner for developing an electrostatic latent image which is capable of forming an image without fogging and which has a high transfer efficiency and an excellent durability.

A further objective of the present invention is to provide a method for forming an image, which allows an excellent minute line reproducibility and gradation, and which is capable of providing an image quality which is equal to or higher than an image obtained by an offset printing, even if a transfer material having a rough surface condition is used.

We have made much effort to study the particle size of coloring particles (the part of a toner exclusive of additives, i.e., the constituent referred to generally as a toner particle) required to achieve the objectives described above. As a result, we have now discovered that a volume average particle size of the coloring particle of $5.0\text{ }\mu\text{m}$ or less is essential for achieving improvement both in the minute line reproducibility and in the gradation of the image.

We also have now discovered that, when using this small-sized coloring particle, the disadvantages associated with the prior art mentioned above can be avoided as a result of the reduction of the size of the coloring particle. In this regard, the aspects of the present invention described below are useful, independently or in combination.

A first aspect of the present invention is thus a coloring particle for use in developing an electrostatic latent image, wherein the coloring particle has a volume average particle size of 1.0 to $5.0\text{ }\mu\text{m}$. Such coloring particle is very effective for achieving improvement in minute line reproducibility, gradation and graininess on highlighted pieces of the obtained image. The coloring particle of the invention is a mixture of coloring particles having different particle sizes. The coloring particles of the invention comprise particles having a particle size of $1\text{ }\mu\text{m}$ or less that are present in an amount of 20% by number or less, and particles having a particle size of more than $5\text{ }\mu\text{m}$ that are present in an amount of 10% by number or less. These particles are mixed with other toner components to achieve a coloring particle (mixture) having a volume average particle size of 1.0 to $5.0\text{ }\mu\text{m}$.

By reducing the volume average particle size of the coloring particle to $5.0\text{ }\mu\text{m}$ or less, the minute line reproducibility, gradation, and graininess on highlight areas will be satisfactory, and deterioration of the minute line reproducibility, gradation, and graininess on highlight area will be reduced or eliminated. Further, increasing the con-

centration of pigment in the coloring particle can decrease the toner weight per unit area of an image formed on a transfer material. Further, since the thickness of the toner image formed on a transfer material can be reduced, an image which is visually appealing and has an equal or higher image quality as that of an image obtained by offset printing can be achieved.

However, it has also been found that only regulating the volume average particle size of the coloring particle is insufficient to achieve a high quality image. For example, the presence of coloring particles having too small of a particle size in a predetermined amount may lead to poor cleanability. On the contrary, the presence of coloring particles having too large of a particle size in a predetermined amount may lead to poor minute line reproducibility. In the present invention, in order to solve the problems of image quality such as fogging and minute line reproducibility, and the problem of poor cleanability, the lower limit of the volume average particle size is about 1.0 μm , coloring particles having a particle size of about 1.0 μm or less are reduced to about 20% by number or less, and coloring particles having a particle size exceeding about 5.0 μm are reduced to about 10% by number or less.

Therefore, with the present invention, an image which has extremely satisfactory minute line reproducibility and gradation and is visually appealing and has an equal or higher image quality to an image obtained by offset printing, and also has satisfactory cleanability, can be obtained.

Furthermore, when an image is formed using the toner for developing an electrostatic latent image of the present invention, the toner weight per unit area of an image formed on a transfer material can be decreased in order to obtain an image having a qualitative impression equal to one obtained by offset printing. In order to achieve a sufficient image density and to keep a good water resistance, light resistance, or solvent resistance of an image even if the toner weight per unit area of an image is decreased, a pigment particle having a high coloring ability and an excellent water resistance, light resistance, or solvent resistance is used as the colorant contained in the coloring particle. A further aspect of the present invention is a toner for developing an electrostatic latent image comprising at least coloring particles containing a colorant and a binder resin, wherein (a) the volume average particle size of the coloring particles is 1.0 to 5.0 μm , preferably wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of 20% by number or less of the entire coloring particles and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less, and (b) the electric charge quantity of said toner for developing electrostatic latent image, q (fC), and the volume average particle size of the toner for developing electrostatic latent image, d (μm), are in such a relationship at the temperature of 20° C., and the humidity of 50% that the peak value and the bottom value q/d in its frequency distribution are 1.0 or less and 0.005 or more, respectively.

In this further aspect, the disadvantages associated with reduction in the size of the coloring particle as described above can be overcome by controlling the state in which individual coloring particles are charged electrostatically. Thus, a toner for developing an electrostatic latent image according to this aspect of the present invention provides an image exhibiting satisfactory minute line reproducibility and gradation while avoiding the disadvantages associated with the prior art mentioned above as a result of the reduction of the size of the coloring particle, such as fogging in a non-image region, reduction in transfer efficiency and retarded charging.

A still further aspect of the present invention is a toner for developing an electrostatic latent image comprising at least coloring particles containing a colorant and a binder resin, and an external additive, wherein

- (a) the volume average particle size of the coloring particles is 1.0 to 5.0 μm , wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of 20% by number or less of the entire coloring particles, and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less,
- (b) the external additive comprises at least one type of ultra microparticles having an average primary particle size of 30 nm to 200 nm and at least one type of super-ultra microparticles having an average primary particle size of 5 nm or more and less than 30 nm, and
- (c) the coating rates, F_a and F_b , of the external additive based on the surface of the coloring particle obtained according to Formula (1) for the ultra microparticles and the super-ultra microparticles, respectively, are both 20% or more, and the total of the coating rate of the entire additive is 100% or less,

$$F = \sqrt{3} \cdot D \cdot \rho_p \cdot (2\pi \cdot z \cdot \rho_a)^{-1} \cdot C \times 100 \quad (1)$$

wherein F denotes a coating rate (%), D denotes the volume average particle size of the coloring particles (μm), ρ_p denotes the true specific gravity of the coloring particles, z denotes the average primary particle size of an additive, ρ_a denotes the true specific gravity of an additive, and C denotes the ratio (x/y) of the weight of the additive, x (g), to the weight of the coloring particles, y (g).

The disadvantages associated with the prior art mentioned above as a result of the reduction of the size of the coloring particle can be prevented by this further aspect of the present invention, i.e., by controlling the particle size distribution of the coloring particles appropriately and additionally by coating the coloring particles with a certain amount of large and small microparticles which are the constituents of the external additive. By this procedure, an image exhibiting satisfactory minute line reproducibility and gradation can be obtained while maintaining the satisfactory powder characteristics such as powder flowability and adhesion ability and avoiding reduction in the transfer efficiency and in the charging ability and also while suppressing the dependency on environment.

While the objectives of the present invention described above can be achieved by using a toner having any of the foregoing aspects of the present invention, a toner for developing an electrostatic latent image which has all of the aspects of the present invention is more preferable for the purpose of achieving a further higher quality of the image and a further higher stability to the environment.

The method for forming an image comprises at least a latent image forming step in which an electrostatic latent image is formed on a latent image support, a toner layer forming step in which a toner layer is formed on the surface of a developer support which faces the electrostatic latent image support, a developing step in which the electrostatic latent image on the electrostatic latent image support is developed with said toner layer, and a transfer step in which a toner image developed is transferred onto a transfer material. A very high quality of an image formed on a transfer material and a high stability to atmosphere throughout the entire image forming process can be achieved with such process by employing a toner for developing an electrostatic latent image according to the present invention in the process.

Especially in a method for forming a full color image by overlaying sequentially in any order the toner images of at least three colors including cyan, magenta and yellow onto the transfer material, or of four colors further including black, improved minute line reproducibility, reduced distortion of the image on the transfer material and reduced image thickness are achieved by employing as each of the three or four color toners a toner for developing an electrostatic latent image according to the present invention, thereby forming an image of a very high quality.

In a still further aspect of the present invention, the method comprises forming a toner layer comprised of toner on a surface of a developer support that is arranged opposed to a latent image support, developing an electrostatic latent image on the latent image support with the toner layer to obtain a toner image, and transferring the toner image formed to a transfer material, wherein the ten-point average surface roughness R_z of at least an image forming region of the transfer material is $10\text{ }\mu\text{m}$ or less and wherein the toner is as described above. To insure the proper surface roughness, the method may include a step of smoothing at least an image-receiving region of a surface of a transfer material before transferring the toner image to the surface of the transfer material. Such smoothing may comprise forming a layer comprising a non-color transparent toner on at least the image-receiving region of the transfer material or forming a layer comprising a white toner on at least the image-receiving region of the transfer material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a schematic perspective view of a device for determining the frequency distribution of the q/d value by the CSG method.

FIG. 2 shows a magnified planar view of a part of the surface of a coloring particle.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is further detailed below by describing the various aspects of the present invention.

A first aspect of the present invention comprises a toner for developing an electrostatic latent image comprising at least coloring particles containing a colorant and binder resin, wherein the coloring particles are a mixture of coloring particles having different average particle sizes, and wherein the volume average particle size of the coloring particles are about 1.0 to about $5.0\text{ }\mu\text{m}$. The coloring particles comprise particles having a particle size of $1.0\text{ }\mu\text{m}$ or less that are present in an amount of 20% by number or less based on the total number of coloring particles, and particles having a particle size exceeding $5.0\text{ }\mu\text{m}$ that are present in an amount of 10% by number or less. The colorant is most preferably a pigment.

Volume average particle size of coloring particles

As described above, it is essential for the improvement in minute line reproducibility and in gradation that the volume average particle size of the coloring particles is $5.0\text{ }\mu\text{m}$ or less. A size exceeding $5.0\text{ }\mu\text{m}$ results in a larger proportion of coarse large particles, which may lead to reduced minute line reproducibility and reduced gradation.

"Minute line reproducibility" referred to herein is intended to mean the ability to reproduce accurately lines formed at an interval of usually 30 to $60\text{ }\mu\text{m}$, preferably 30 to $40\text{ }\mu\text{m}$. The evaluation of the minute line reproducibility also considers the ability to reproduce a dot having a

diameter within the above size range, i.e., a dot having the same width as the minute line. The evaluation is further described below in the examples.

It is also essential that the lower limit of the volume average particle size of the coloring particles is $1.0\text{ }\mu\text{m}$ or more. A size less than $1.0\text{ }\mu\text{m}$ results in deterioration of the flowability of the powder as a toner, developability or transfer ability, which may lead to various problems associated with poor powder characteristics, such as reduced cleanability of the toner remaining on the surface of a photoconductor.

Based on the discussion made above, the volume average particle size of the coloring particles is preferable within the range from 1.0 to $4.5\text{ }\mu\text{m}$, more preferably 1.0 to $4.0\text{ }\mu\text{m}$ or 2.0 to $3.5\text{ }\mu\text{m}$, most preferably 3.0 to $3.5\text{ }\mu\text{m}$.

The particle size of the coloring particles is further specified in this aspect of the present invention. Typically, it is essential that coloring particles having a particle size of $1.0\text{ }\mu\text{m}$ or less are present in an amount of 20% by number or less of the entire coloring particles, and coloring particles having a particle size exceeding $5.0\text{ }\mu\text{m}$ are present in an amount of 10% by number or less.

When reducing the size of the coloring particle, if small-sized coloring particles, for example having a size of $1.0\text{ }\mu\text{m}$ or less, are present in a predetermined amount or more, for example, more than 20% by number, fogging may occur on a non-image area, and cleanability may be deteriorated. On the other hand, if a large-sized coloring particle, for example having a size of $5.0\text{ }\mu\text{m}$ or more, is present in a predetermined amount or more, for example more than 10% by number, the minute line reproducibility may be rendered insufficient. These disadvantages are prevented by controlling the particle size distribution of the coloring particle appropriately with respect to the above-described toner.

When coloring particles having a particle size of $1.0\text{ }\mu\text{m}$ or less are present in an amount exceeding 20% by number of the entire coloring particle, fogging in a non-image region and poor cleaning may occur since the non-electrostatic adhesive force of the coloring particles is increased.

More preferably, coloring particles having a particle size of $1.0\text{ }\mu\text{m}$ or less are present in an amount of 10% by number or less of the entire coloring particle. When the number of coloring particles having a particle size of $1.0\text{ }\mu\text{m}$ or less of the entire coloring particle is in the above range, fogging is reduced.

Furthermore, when coloring particles having a particle size exceeding $5.0\text{ }\mu\text{m}$ are present in an amount exceeding 10% by number, improvement in minute line reproducibility as an object of the present invention may not be achieved.

More preferably, coloring particles having a particle size exceeding $5.0\text{ }\mu\text{m}$ are present in an amount of 5% by number or less.

While the percentage by number of coloring particles having the size exceeding $5.0\text{ }\mu\text{m}$ is employed as a parameter for specifying the larger limit of the particle size distribution of the coloring particle in the present invention, the particle size employed as a basis can also be specified by other values. For example, when the basis of the particle size is $4.0\text{ }\mu\text{m}$, it is preferable that coloring particles having a particle size of $4.0\text{ }\mu\text{m}$ or less are present in an amount of 75% by number or more. In view of the volume average particle size and the particle size distribution of a coloring particle according to the present invention, when coloring particles having a particle size of $4.0\text{ }\mu\text{m}$ or less are present in an amount of 75% by number or more, then coloring particles having a particle size exceeding $5.0\text{ }\mu\text{m}$ is generally present in an amount of 10% by number or less.

It is also preferable that coloring particles having particle sizes of 1.0 μm to 2.5 μm are present in an amount of 5% to 50% by number, more preferably 10% to 45% by number. When coloring particles having a particle size of 1.0 μm to 2.5 μm are present in an amount exceeding 50% by number, small size particles remain in the developer and fogging may occur.

On the other hand, when coloring particles having a particle size of 1.0 μm to 2.5 μm are present in an amount less than 5% by number, minute dot reproducibility may deteriorate.

For obtaining a coloring particle having the particle size distribution described above, the conditions of pulverizing and classification (in the case of pulverization) and the conditions of polymerization (in the case of polymerization) may be any appropriate conditions. To achieve the particle distribution of the invention, pulverization is preferable. Pulverization allows the production of very small particles that are easy to classify, and simple and inexpensive to produce. Such pulverization method involves premixing of a binder resin and a colorant as well as other additives if necessary, followed by melting in a kneader, followed by cooling, grinding and classification to adjust to the particle distribution. Suitable methods are also illustrated in the Examples below.

While the particle size distribution of coloring particles may be determined by various methods, a Coulter counter model TA II (manufactured by Coulter Co., Ltd.) with the aperture size of 50 μm , except for 30 μm which is employed only when determining the number distribution of toner particles of 1 μm or less, is employed in the present invention. The device outputs the particle size and size distribution directly.

Typically, 2 to 3 drops of a dispersing agent (surfactant: Triton X 100) and a sample are placed in an aqueous solution of sodium chloride (10 g/liter) and dispersed ultrasonically for 1 minute and then subjected to the determination using the device described above.

A further aspect of the present invention is a toner for developing an electrostatic latent image comprising coloring particles containing a colorant and a binder resin (hereinafter sometimes simply referred to as "toner"), wherein

- (a) the volume average particle size of the coloring particles is 1.0 to 5.0 μm , and
- (b) the electric charge quantity of said toner for developing an electrostatic latent image, q (fC), and the volume average particle size of the toner/coloring particles for developing an electrostatic latent image, d (μm), are in such a relationship at the temperature of 20° C. and the humidity of 50% that the peak value and the bottom value of q/d in its frequency distribution are 1.0 or less and 0.005 or more, respectively.

In this aspect of the present invention, the volume average particle size of the coloring particles is the same as discussed above with respect to the first aspect of the invention. Also, while the particle size distribution in this further aspect of the invention is preferably the same as that discussed above in the first aspect, it is not essential to this aspect. In other words, in this further aspect of the invention, it is sufficient that the volume average particle size of the coloring particles be 1.0 to 5.0 μm , regardless of the particle size distribution.

Relationship between electric charge quantity, q , and particle size d (q/d value)

Controlling the state of the charging of individual coloring particles appropriately can prevent the disadvantages associated with the prior art mentioned above as a result of

the reduction of the size of the coloring particle. Thus, the image obtained depends greatly on the state of the charging of an individual toner particle rather than on the quantity of the entire electric charge quantity. On the other hand, the image quality depends also on the size of an individual toner particle, and thus the relationship with the image quality cannot sufficiently be explained based only on the specified frequency distribution of the electric charge quantity of an individual toner particle. Accordingly, in this aspect of the present invention, the relationship between the electric charge quantity and the volume average particle size of an individual toner particle is specified appropriately.

Thus, in this aspect of the present invention, the electric charge quantity of said toner for developing electrostatic latent image, q (fC), and the volume average particle size of the coloring particles for developing electrostatic latent image, d (μm), are in such a relationship at the temperature of 20° C. and the humidity of 50% that the peak value and the bottom value of q/d in its frequency distribution are 1.0 or less and 0.005 or more, respectively. The disadvantages due to the reduction in the size of the coloring particle as described above, e.g., fogging in a non-image region, reduction in transfer efficiency and retarded charging, can be overcome by controlling the charging condition of the individual coloring particles suitably in such a way.

While the q/d value of a positively charged toner can directly be applied to the specified value of this aspect of the present invention, that of a negatively charged toner can be applied to the specified value of this aspect of the present invention after positive-negative inversion of the value of the electric charge quantity of a toner for developing an electrostatic latent image, q (fC).

In this aspect of the present invention, the peak value of q/d in its frequency distribution is preferably 0.8 or less, and the bottom value is preferably 0.01 or more.

The reason why the temperature 20° C. and the humidity 50% are specified as the condition under which the electric charge quantity is determined is that the electric charge quantity is specified most appropriately at room temperature which is regarded as a normal environment for the purpose of achieving various performances as the objectives of the present invention. Thus, a toner for developing an electrostatic latent image according to the present invention which fulfills the requirements described above in the normal environment does not undergo a substantial deviation from the appropriate electric charge distribution for obtaining an intended high image quality even when the environmental condition becomes somewhat different, thus exhibiting an extremely stable and high performance. It is a matter of course that a toner for developing an electrostatic latent image which maintains the electric charge distribution described above even at a higher temperature and a higher humidity or at a low temperature and a low humidity is preferable.

When the q/d value of an individual toner for developing an electrostatic latent image is determined and then its frequency distribution is represented as a graph, an approximately normal distribution having an upper limit and a lower limit can be obtained. In this aspect of the present invention, the q/d value at the maximum point of this graph is designated as the peak value, while the q/d value at the lower limit (in the case of a negatively charged toner, the lower limit after positive-negative inversion) is designated as the bottom value.

In this aspect of the present invention, it is essential for the peak value of the q/d in the frequency distribution to be 1.0 or less, preferably 0.80 or less, more preferably 0.70. A peak

value exceeding 1.0 results in an increased adhesive force of the toner onto the surface of a carrier or a photoconductor even at a narrow frequency distribution, and thus causes deterioration of developability and transferability, reduced image density, as well as significantly reduced cleanability of the toner remaining on the photoconductor. A peak value exceeding 1.0 at a broad electric charge distribution results in the problems described above in combination with uneven development and transfer performances due to the increased deviation in the charge of the toner.

When the q/d value is too close to zero or is a positive-negative inverted value (i.e., a counter-polarly charged toner), a blank area in the image region or a fogging in a non-image region may occur. Accordingly, the bottom value in the frequency distribution of the q/d value should be maintained at a certain value or higher, and thus should typically be 0.005 or higher, preferably 0.01 or higher, more preferably 0.02 or higher, particularly 0.025 or higher.

In this aspect of the present invention, the upper limit of the q/d value in the frequency distribution (the upper limit as the absolute value in the case of a negatively charged toner) is not particularly specified. The frequency distribution of the q/d value is an approximately normal distribution as described above, and the upper limit becomes apparent spontaneously when specifying the peak value and the bottom value.

The frequency distribution of the q/d value can be determined by the Charge Spectrograph method (hereinafter referred to as CSG method) shown, for example, in Japanese Patent Application Laid-Open No. 57-79958, incorporated herein by reference. The method for determination is detailed below.

FIG. 1 shows a schematic perspective view of device 10 for determining the frequency distribution of the q/d value by the CSG method. Device 10 consists of cylindrical body 12 with its lower opening closed with filter 14 and its upper opening closed with mesh 16, sample supply cylinder 18 protruding through the middle of mesh 16 into the inside of body 12, a suction pump (not indicated) for sucking air via the lower opening of body 12, and a electric field generating device (not indicated) providing electric field E from the side wall of body 12.

The suction pump is provided to suck air contained in body 12 through the entire surface of filter 14 which is engaged in the lower opening of body 12. At the same time, air is introduced through mesh 16 fitted to the upper opening, whereby a laminar flow of air downward vertically in body 12 at a constant flow rate V_a is established. The electric field generating device provides a uniform and constant field E in the direction of a right angle with regard to the air flow.

To the inside of body 12 in the state described above, a toner particle to be determined is dropped (allowed to fall down) via sample supply cylinder 18. The toner particle exiting from sample exit 20 at the terminal of the sample supply cylinder 18 flies when not being subjected to electric field E vertically downward while being influenced by the laminar air flow, and arrives at center O of filter 14 (in this case the distance K between sample exit 20 and filter 14 is the straight flight distance of the toner). Filter 14 is made from a coarse mesh polymer filter, through which air can readily pass but the toner particle cannot, resulting in the toner left on filter 14. When the toner is electrically charged, it is subjected to the effect of electric field E, and arrives on filter 14 at a point deviated from center O in the direction of electric field E (point T in FIG. 1). By determining the distance x (shift) between point T and point O and obtaining

frequency distribution, the frequency distribution of the q/d value can be obtained. In the present invention, the image analysis is employed to obtain the peak value and the bottom value.

Typically, the shift obtained using device 10, x (mm), the electric charge quantity of the toner, q (fC) and the particle size of the toner, d (μm), are in the relationship represented by formula (3).

$$q/d = (3\pi\eta V_a/kE)x \quad (3)$$

wherein η represents the viscosity of air (kg/m-sec), V_a represents air flow rate (m/sec), k represents the straight flight distance of a toner (m), and E represents the electric field (V/m).

In the present invention, device 10 shown in FIG. 1 is adjusted to such a condition that the parameters in formula (3) are as shown below.

Viscosity of air $\eta = 1.8 \times 10^{-5}$ (kg/m-sec)

Air flow rate $V_a = 1$ (m/sec)

Straight flight distance of toner $k = 10$ (cm)

Electric field $E = 190$ V/cm

When the values indicated above are applied to formula (3), the following value is obtained.

$$q(\text{fC})/d(\mu\text{m}) = 0.09 \cdot x$$

Before the particle of a toner for developing an electrostatic latent image to be subjected to the determination is allowed to fall down through sample supply cylinder 18, it should be charged electrically. The q/d value of a toner for developing an electrostatic latent image should be in the frequency distribution described above when the electrostatic latent image is developed actually, and thus for the purpose of the present invention the toner for developing an electrostatic latent image to be subjected to determination is first mixed with a carrier to form a two-component developer, which is then treated in the condition analogous to that of the device, for example, by agitation prior to being subjected to the determination of the frequency distribution of the q/d value.

Accordingly in the present invention, the charging condition of a toner particle for developing an electrostatic latent image to be subjected to the determination is specified as described below. It is more preferable as a matter of course that the toner for developing an electrostatic latent image which is sampled directly from the device upon developing the electrostatic latent image fulfills the requirement with regard to the frequency distribution of the q/d described above.

In the present invention, a practically employed developer for an electrostatic latent image which comprises a toner for developing an electrostatic latent image and a carrier is placed in a glass container and stirred for 2 minutes using a turbulor shaker to effect the charging, and then evaluating for the frequency distribution of the q/d .

As described above, the frequency distribution of the q/d value can be obtained. While the frequency distribution of the q/d value may be determined in the present invention by any other method instead of the CSG method described above, less error is associated with the CSG method.

For producing a toner for developing an electrostatic latent image according to this aspect of the present invention, an external additive may be admixed with the coloring particle for the purpose of controlling the charging. The q/d value may thus be suitably adjusted to be within the required parameters through addition of an external additive.

An inorganic fine powder material employed as such external additive may be, for example, metal oxides such as titanium oxide, tin oxide, zirconium oxide, tungsten oxide, iron oxide and the like, nitrides such as titanium nitride and the like, as well as silicon oxide and titanium compounds. The amount of an external additive to be added is preferably 0.05 to 10 parts by weight, more preferably 0.1 to 8 parts by weight, based on 100 parts by weight of a coloring particle.

For adding an inorganic fine powder mentioned above to a toner, a known method may be employed such as placing the inorganic fine powder and a coloring particle in a Henschel mixer and mixing them.

A preferred method of producing a toner for developing an electrostatic latent image according to this aspect of the present invention constitutes a still further aspect of the present invention. This further aspect of the present invention allows the frequency distribution of the q/d value to be controlled appropriately.

This further aspect of the present invention is a toner for developing an electrostatic latent image comprising a coloring particle containing a colorant and a binder resin, and an external additive, wherein

- (a) the volume average particle size of the coloring particles is 1.0 to 5.0 μm , wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of 20% by number or less of the entire coloring particle, and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less,
- (b) the external additive comprises at least one type of ultra microparticles having an average primary particle size of 30 nm to 200 nm and at least one type of super-ultra microparticles having an average primary particle size of 5 nm or more and less than 30 nm, and
- (c) the coating rates, Fa and Fb, of the external additive based on the surface of the coloring particle obtained according to Formula (1) for the ultra microparticles and the super-ultra microparticles, respectively, are both 20% or more, and the total of the coating rate of the entire additive is 100% or less,

$$F = \sqrt{3} \cdot D \cdot \rho_c \cdot (2\pi \cdot r \cdot \rho_a)^{-1} \cdot C \times 100 \quad (1)$$

wherein F denotes a coating rate (%), D denotes the volume average particle size of the coloring particles (μm), ρ_c denotes the true specific gravity of the coloring particles, z denotes the average primary particle size of an additive, ρ_a denotes the true specific gravity of an additive, and C denotes the ratio (x/y) of the weight of the additive, x (g), to the weight of the coloring particles, y (g).

By "type of" ultra microparticles is meant that the ultra microparticles may be of the same or different composition. Suitable example types of ultra microparticles are set forth below. Similarly, by "type of" super-ultra microparticles is meant that the super-ultra microparticles may be of the same or different composition. Suitable example types of super-ultra microparticles are set forth below.

The external additive also makes the small-sized toner more stable and maintains the high handling ability of the toner.

The volume average particle size and particle size distribution of the coloring particles in this further aspect of the present invention is identical to the first aspect discussed above.

Thus, the volume average particle size of the coloring particles is 1.0 to 5.0 μm , wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of

20% by number or less of the entire coloring particle, and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less. The significance and advantages associated with coloring particles having such a volume average particle size and particle size distribution are identical to those discussed in conjunction with the first aspect above.

Particle size of two external additive particles

In this further aspect of the present invention, at least one type of ultra microparticles having an average primary particle size of 30 nm to 200 nm and at least one type of super-ultra microparticles having an average primary particle size of 5 nm or more and less than 30 nm are employed as an external additive.

The ultra microparticles serve to reduce the adhesion between coloring particles or between a coloring particle and a photoconductor or a carrier, and to prevent the reduction in developability, transferability or cleanability. The average primary particle size of an ultra microparticle according to the second aspect of the present invention is 30 nm to 200 nm, preferably 35 nm to 150 nm, and more preferably 35 nm to 100 nm. When exceeding 200 nm, release from a toner may readily occur, resulting in absence of adhesive force-reducing effect. On the other hand, a particle having a size less than 30 nm serves rather as a super-ultra microparticle which is detailed below.

The super-ultra microparticles impart a toner (coloring particle) with an improved flowability and a reduced aggregation degree while serving to improve the environmental stability as a result of the effects such as suppression of heat aggregation. The average primary particle size of a super-ultra microparticle according to the second aspect of the present invention is 5 nm or more and less than 30 nm, preferably 5 nm or more and less than 29 nm, and more preferably 10 nm to 29 nm. A size less than 5 nm may result in embedding in the surface of a coloring particle due to the stress given to a toner. On the other hand, a particle having a size of 30 nm or more serves rather as an ultra microparticle described above.

In the present invention, the term "primary particle" means the primary particle size of a particle as a spherical particle. In other words, a non-spherical particle having a volume is converted via known calculations to a corresponding perfectly spherical particle of the same volume. Then, the size (i.e., diameter) of this perfectly spherical particle is determined. The average primary particle size of the additives are typically determined with the use of a scanning electronic microscope in a manner known in the art. The average primary particle size of the additives are thus reported on a number basis.

The types of ultra microparticles may include, for example, metal oxides such as hydrophobicity-imparted silicon oxide, titanium oxide, tin oxide, zirconium oxide, tungsten oxide, iron oxide, nitrides such as titanium nitride, and microparticles containing titanium compounds, with a microparticle comprising hydrophobicity-imparted silicon oxide being preferred. The hydrophobicity may be imparted by treatment with a hydrophobicity-imparting agent, such as for example, chlorosilane, alkoxysilane, silazane, silylated isocyanate and the like. For example, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, methyltrimethoxysilane, dimethyldimethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, i-butyltrimethoxysilane, decyltrimethoxysilane, hexamethyldisilazane, t-butyltrimethylchlorosilane, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane and the like may be employed.

The types of super-ultra microparticles may include, for example, microparticles comprising metal oxides such as hydrophobic titanium compound, silicon oxide, titanium oxide, tin oxide, zirconium oxide, tungsten oxide, iron oxide and nitrides such as titanium nitride, with a titanium compound microparticle being preferred.

As a titanium compound microparticle, a reaction product between metatitanic acid and a silane compound is preferable since it is highly hydrophobic, less of it tends to form aggregations due to no sintering process being required, and it exhibits satisfactory dispersibility when added as an external additive. As the silane compound, an alkylalkoxysilane compound and/or a fluoroalkylalkoxysilane compound is preferably employed since it satisfactorily controls the charging of a toner, and reduces the adhesion to a carrier and a photoconductor.

The metatitanic acid compound thus preferably is a reaction product between metatitanic acid and an alkylalkoxysilane compound and/or a fluoroalkylalkoxysilane compound. The compound is preferably obtained by peptizing metatitanic acid synthesized by sulfuric acid hydrolysis followed by reacting the peptized metatitanic acid as a base with the alkylalkoxysilane compound and/or the fluoroalkylalkoxysilane compound.

The alkylalkoxysilane compound to be reacted with metatitanic acid includes, for example, methyltrimethoxysilane, ethyltrimethoxysilane, propyltrimethoxysilane, i-butyltrimethoxysilane, n-butyltrimethoxysilane, n-hexyltrimethoxysilane, n-octyltrimethoxysilane, n-decyltrimethoxysilane and the like, and the fluoroalkylalkoxysilane compound includes, for example, trifluoropropyltrimethoxysilane, tridecafluorooctyltrimethoxysilane, heptadecafluorodecyltrimethoxysilane, heptadecafluorodexylmethyldimethoxysilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane, (3,3,3-trifluoropropyl)trimethoxysilane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane, 3-(heptafluoroisopropoxy)propyltriethoxysilane and the like.

Coating rate of two external additive components on coloring particle surface

As described above, by using at least two external additive components, i.e., ultra microparticles and super-ultra microparticles, a toner for developing an electrostatic latent image according to this further aspect of the present invention should be imparted with the combined effects as a result of combination of the both components.

Nevertheless, when an excessive amount in total of an external additive is added, a part of the external additive is present as liberated from (i.e., as not adhering to) a coloring particle and the surface of a photoconductor or a carrier becomes stained readily with the external additive. On the other hand, ultra microparticles and super-ultra microparticles should be present both in at least certain amounts for obtaining the effects as a result of the combination of both. An excessive amount of ultra microparticles results in the absence of powder flowability-improving effect, while an excessive amount of super-ultra microparticles results in a poor powder flowability as well as the absence of powder flowability-improving effect. Accordingly, the amount of an external additive to be added should be appropriately controlled.

However, the effects and the variation in various powder characteristics as a result of addition of an external additive is not dependent on the absolute amount of the external additive added, but is instead dependent on the coating rate

on the surface of a coloring particle. The coating rate of an external additive on the surface of a coloring particle is discussed below.

If an external additive component is regarded as a true sphere (diameter: z) and a non-aggregated primary particle adheres as a monolayer to the surface of a coloring particle, then the most dense packing of the external additive adhering to the surface of the coloring particle (in the state in which the particle is aligned as closely packed) is represented as a hexagonal close-packed structure in which six external additive units 22a to 22f are all adjacent to one external additive unit 22 as shown in FIG. 2 (FIG. 2 shows a planar view of a magnified part of the surface of the coloring particle).

Assuming that the state shown in FIG. 2 represents an ideal 100% coating, the actual weight of the external additive based on the actual weight of the coloring particle is represented as present, which is designated herein as the coating rate.

Thus, in an actual state, when designating the volume average particle size of the coloring particles as D (μm), the true specific gravity of the coloring particles as ρ_c , the average primary particle size of an additive as z (μm), the true specific gravity of an additive as ρ_o , the ratio (x/y) of the weight of the additive, x (g), to the weight of the coloring particles, y (g) as C , then the coating rate F (%) may be represented as:

$$F = C / \{ 2\pi z \rho_o / (\sqrt{3} D \rho_c) \} \times 100$$

which can be converted to:

$$F = \sqrt{3} D \rho_c (2\pi z \rho_o)^{-1} \cdot C \times 100 \quad (1)$$

wherein F denotes a coating rate (%), D denotes the volume average particle size of the coloring particles (μm), ρ_c denotes the true specific gravity of the coloring particles, z denotes the average primary particle size of an additive, ρ_o denotes the true specific gravity of an additive, and C denotes the ratio (x/y) of the weight of the additive, x (μ), to the weight of the coloring particles, y (g).

In this further aspect of the present invention, the coating rates of both components of the external additive, i.e., ultra microparticles and super-ultra microparticles, on the surface of a coloring particle obtained according to Formula (1) as discussed above, namely, F_a and F_b , should be 20% or more, with the total coating rate of the entire additive being 100% or less.

The expression "the total coating rate of the entire additive" means the sum of all coating rates of all external additive components, each of which is calculated independently.

When the coating rate of ultra microparticles, F_a , is less than 20%, no effects of the addition of the ultra microparticle is obtained. The coating rate of ultra microparticles, F_a , is preferably 20 to 80%, more preferably 30 to 60%.

When the coating rate of super-ultra microparticles, F_b , is less than 20%, no effects of the addition of the super-ultra microparticle is obtained. The coating rate of super-ultra microparticles, F_b , is preferably 20 to 80%, more preferably 30 to 60%.

When the total coating rate of the entire additive exceeds 100%, an increased external additive may be liberated and the surface of a photoconductor or a carrier becomes stained readily with the external additive. The total coating rate of the entire additive is preferably 40 to 100%, more preferably 50 to 90%.

For the purpose of obtaining more appropriate powder characteristics and eliminating the dependency on

environment, the coating rate of ultra microparticles, Fa (%), and the coating rate of super-ultra microparticles, Fb (%), are preferably in the relationship represented by Formula (2).

$$0.5 \leq Fb/Fa \leq 4.0 \quad (2)$$

The relationship departing from this range is not preferable since it may become difficult to obtain the effect of the addition of the ultra microparticle or the super-ultra microparticle.

For obtaining an optimum effect of the addition of the ultra microparticle or the super-ultra microparticle, it is preferable that Formula (2') shown below be satisfied.

$$0.5 \leq Fb/Fa \leq 2.5 \quad (2')$$

For adding an ultra microparticle and a super-ultra microparticle to a toner, a known method may be employed such as placing the ultra microparticle and the super-ultra microparticle and a coloring particle in a Henschel mixer and mixing them.

In this aspect, it is also preferable that 75% by number of the entire coloring particles preferably have a particle size of 4.0 μm or less.

In addition to the common features among the various aspects of the present invention discussed above, following are further additional features of the invention that may be common among all of the various aspects of the present invention.

Coloring particle

A coloring particle according to the present invention (hereinafter "the present invention" is intended to refer to all of the various aspects of the present invention) contains at least a binder resin and a colorant.

The binder resin contained in a coloring particle preferably has a glass transition point which is, for example, 50 to 80° C., more preferably 55 to 75° C. A glass transition point below 50° C. may cause a disadvantageously reduced high temperature storage stability, while that higher than 80° C. may cause a reduced low temperature fixing ability, which is also disadvantageous.

The softening point of a binder resin is preferably, for example, 80 to 150° C., more preferably 90 to 150° C., and most preferably 100 to 140° C. A softening point below 80° C. may cause a disadvantageously reduced high temperature storage stability, while that higher than 150° C. may cause a reduced low temperature fixing ability, which is also disadvantageous.

The number average molecular weight of a binder is preferably, for example 1,000 to 50,000, while the weight average molecular weight of a binder is preferably, for example, 7,000 to 500,000.

A binder resin may be any one of those employed conventionally as a binder resin for a toner, such as, for example, styrenic polymers and (meth)acrylate polymers. A styrene-(meth)acrylate polymer is preferably obtained by polymerizing one or more of the styrene monomers, (meth)acrylate monomers, other acrylic or methacrylic monomers, vinyl ether monomer, vinyl ketone monomer, or N-vinyl compound monomers listed below.

Styrenic monomers include, for example, styrene and styrene derivatives such as o-methylstyrene, ethylstyrene, p-methoxystyrene, p-phenylstyrene, 2,4-dimethylstyrene, p-n-octylstyrene, p-n-decylstyrene, p-n-dodecylstyrene, butylstyrene and the like.

(Meth)acrylate monomers include, for example, (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)

acrylate, propyl (meth)acrylate, butyl (meth)acrylate, i-butyl (meth)acrylate, n-octyl (meth)acrylate, dodecyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyl (meth)acrylate, phenyl (meth)acrylate, dimethylaminoethyl (meth)acrylate and the like.

Other acrylic or methacrylic monomers include, for example, acrylonitrile, methacrylamide, glycidyl methacrylate, N-methylol acrylamide, N-methylol methacrylamide, 2-hydroxyethyl acrylate and the like.

Vinylether monomers include, for example, vinyl ethers such as vinylmethylether, vinyl ethylether, vinyl i-butylether and the like.

Vinylketone monomers include, for example, vinylketones such as vinylmethylketone, vinylhexylketone, methyl i-propenylketone and the like. N-vinyl compound monomers include, for example, N-vinyl compounds such as N-vinylpyrrolidone, N-vinylcarbazole, N-vinylindole and the like. In the present invention, a polyester may preferably be employed as a binder resin in view of fixing ability. Such polyester may be one synthesized by condensation polymerization of a polycarboxylic acid and a polyhydric alcohol.

Polyhydric alcohol monomers are, for example, aliphatic alcohols such as ethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol, 2,3-butane diol, diethylene glycol, 1,5-pentane diol, 1,6-hexane diol and neopentyl glycol, alicyclic alcohols such as cyclohexane dimethanol and hydrogenated bisphenol, bisphenol derivatives such as bisphenol A ethylene oxide adduct and bisphenol A propylene oxide adduct. Polycarboxylic acids are, for example, aromatic carboxylic acids and anhydrides thereof such as phthalic acid, terephthalic acid, phthalic anhydride, and saturated and unsaturated carboxylic acids and anhydrides thereof such as succinic acid, adipic acid, sebacic acid, azelaic acid and dodecenyl succinic acid.

The colorant contained in a coloring particle may be any known pigment or dye. If the amount of a colorant added is excessive, the charging characteristics of the toner is affected adversely. Because of this, a pigment which develops a color intensely even when added at a low level is preferably employed in the present invention. In particular, as the colorant contained in the coloring particles in order to achieve a sufficient image density even if the toner weight per unit area of an image is lowered and to keep water resistance, light resistance or solvent resistance of an image, a pigment particle which has a high coloring ability and is excellent in water resistance, light resistance, or solvent resistance, is preferably used.

Examples of suitable pigments include carbon black, nigrosine, graphite, C.I. Pigment Red 48:1, 48:2, 48:3, 53:1, 57:1, 112, 122, 123, 5, 139, 144, 149, 168, 177, 178, 222, C.I. Pigment Yellow 12, 14, 17, 97, 180, 188, 93, 94, 138, 174, C.I. Pigment Orange 31, C.I. Pigment Orange 43, C.I. Pigment Blue 15:3, 15, 15:2, 60, C.I. Pigment Green 7 and the like, and among these, carbon black, C.I. Pigment Red 48:1, 48:2, 48:3, 53:1, 57:1, 112, 122, 123, C.I. Pigment Yellow 12, 14, 17, 97, 180, 188, C.I. Pigment Blue 15:3 are especially preferred. These pigments may be employed individually or in combination.

A method for employing a pigment microparticle after reducing the average disperse size of the toner colorant in the binder resin to 0.3 μm or less as a circle diameter by means of a melt flushing method for the purpose of improving the coloring ability and the transparency of a color toner has been proposed (Japanese Patent Application No. 4-242752, incorporated herein by reference), and this method is very useful for the toner for developing an electrostatic latent image according to the present invention in which the colorant density in the coloring particle should be high.

The melt flushing method, which is a means to disperse a pigment particle in a binder resin, involves replacement of the water contained in a hydrated pigment cake during a pigment manufacturing process with a molten binder resin, and by this method it is easy to reduce the average disperse size of the pigment microparticle in the binder resin to 0.3 μm or less as a circle diameter, and the use of such small-sized pigment microparticles allows the transparency of the toner to be ensured advantageously, resulting in satisfactory color reproduction.

In a toner for developing an electrostatic latent image according to the present invention, the coloring particles have a volume average particle size of 5.0 μm or less and the coloring ability of a single particle of the coloring particles should be high. Especially in a full color image in which coloring particles are overlaid and developed on a transfer material, an insufficient transparency of the coloring particles may allow the coloring particles in the upper layer to shield the color of the lower layer upon forming a two colored image such as a red and green image or a three colored image as of a process black, but such problem can be solved by reducing the average disperse size of the colorant pigment in the binder resin to 0.3 μm or less as a circle diameter.

As described above, a toner for developing an electric latent image has a small particle size and cannot provide a sufficient image density at a pigment concentration similar to that for a conventional large sized toner. Although a toner for developing an electric latent image may simply be described to have a small particle size, the size varies widely from 1.0 μm to 5.0 μm , and may result in a substantial difference in the weight of the toner per unit area (TMA) of a solid image. Accordingly, it is desirable that the concentration of a pigment required is selected based on TMA.

Assuming that a toner is deposited as a monolayer on a transfer material, TMA is dependent on the volume average particle size, D (μm), and the specific gravity, a , of the coloring particles, and the concentration of pigment in a coloring particle, C (%). These parameters preferably fulfill the relationship represented by Formula (4) shown below.

$$25 \leq a \cdot D \cdot C \leq 90 \quad (4)$$

An $a \cdot D \cdot C$ (hereinafter abbreviated as aDC) less than 25 may result in an insufficient coloring ability which leads to difficulty in obtaining a desired image density, and an attempt to obtain the desired image density by increasing the amount of the toner upon development may result in a glossy and thicker image in spite of a small particle size, and also may cause disadvantageous reduction in minute line reproducibility and in transfer ability.

On the other hand, an $a \cdot D \cdot C$ exceeding 90 gives a satisfactory image density but may cause such a disadvantage that a soiled background may readily be formed due to the splash of a small amount of a toner to a non-image region and that the reinforcing effect of a pigment may increase the melt viscosity of a coloring particle which leads to a poor fixing ability.

The coloring ability also varies color by color, and each color is preferably in accordance with the following formulae (4-1) to (4-4).

Cyan:	$25 \leq a \cdot D \cdot C \leq 90$	(4-1)
Magenta:	$25 \leq a \cdot D \cdot C \leq 60$	(4-2)
Yellow:	$30 \leq a \cdot D \cdot C \leq 90$	(4-3)
Black:	$25 \leq a \cdot D \cdot C \leq 60$	(4-4)

Since the pigments even of an identical color may have different coloring abilities due to the difference in chemical

structures or other factors, the concentration of a pigment may vary depending on the types of the pigment, preferably within the range specified above.

Any known method such as pulverization or polymerization such as suspension polymerization or emulsion polymerization may produce a coloring particle, although pulverization is preferable in the present invention as already described. Such pulverization method involves premixing of a binder resin and a colorant as well as other additives if necessary, followed by melting in a kneader, followed by cooling, grinding and classification to adjust to a certain particle distribution.

Other additives to toner for developing electrostatic latent image

As far as color reproducibility or transparency is not affected adversely, additives such as charge controlling agents and release agents may be added if desired to a toner for developing an electric latent image according to the present invention. Examples of the charge controlling agents are chromium-based azo dyes, silver-based azo dyes, aluminum azo dyes, metal salicylate complexes, organic boron compounds and the like. Examples of the release agents are polyolefins such as low molecular weight propylenes and low molecular weight polyethylenes, and naturally-occurring waxes such as paraffin wax, candelilla wax, carnauba wax, montan wax as well as the derivatives thereof.

Aggregation degree of toner for developing electric latent image

The aggregation degree of a toner for developing an electrostatic latent image according to the present invention is preferably 30 or less, more preferably 25 or less, particularly 20 or less. The aggregation degree is an index for the aggregating force between toners and a larger value indicates a larger aggregation force between toners.

In the present invention, by specifying the aggregation degree to be 30 or less, reduction in flowability due to the reduced size of a toner and reduction of dispersibility in a carrier can be minimized, and a soiled background and a reduced image density as a result of insufficient toner supply, retarded charging, poor charge distribution and reduced charge as well as the stability during storage can also be improved. An aggregation degree of a toner exceeding 30 may result in a soiled background due to reduced flowability and reduced dispersibility in a carrier and an uneven image due to reduced density as well as a poor stability during storage. According to the aspect of the present invention in which the coating rate of external additive particles is controlled as discussed above, the balance between the particle size and the coating rate of an external additive allows the aggregation degree to be extremely low.

The aggregation degree may be determined using a powder tester (manufactured by HOSOKAWA MICRON). Typically, the following procedure may be employed.

Sieves of 45 μm mesh size, 38 μm mesh size and 26 μm mesh size are placed in a low and in this order and 2 g of a toner, accurately weighed, is loaded onto the top 45 μm sieve, to which then 1 mm oscillation is given for 90 seconds, after which the toner of each sieve is weighed and each weight is multiplied by 0.5, 0.3 and 0.1 in the order of the heaviness, and the values obtained are then multiplied by 100. In the present invention, a sample is allowed to stand for about 24 hours at 22° C. and 50% RH, and determined at 22° C. and 50% RH.

Developer for electrostatic latent image

A toner for developing an electrostatic latent image according to the present invention is preferably mixed with a carrier and used as a two component developer for an electrostatic latent image.

The carrier which is suitable to be combined with a toner for developing an electrostatic latent image according to the present invention is not particularly limited and may be, for example, magnetic particles such as iron powder, ferrite, iron oxide powder, nickel and the like, resin-coated carrier particles formed by coating the surface of a magnetic particles as a core material with a known resin such as styrenic resins, vinylic resins, ethyl-based resins, rosin-based resins, polyester-based resins, methyl-based resins and the like or with waxes such as stearic acid to form a resin coating layer, as well as carrier particles containing magnetic substance dispersed therein.

Resin-coated carrier particles having resin coating layers are particularly preferable since the resin coating layers serve to control the charging performance of a toner and the resistance of the entire carrier.

Materials for the resin coating layer may be selected widely from the resins usually employed as materials for the resin coating layer for the carriers. Such resins may be employed independently or in combination. Examples include polyethylene, polypropylene, polystyrene, polyacrylonitrile, polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, polyvinyl chloride, polyvinyl carbazol, polyvinyl ether, polyvinyl ketone, vinyl chloridevinyl acetate copolymer, styrene-acrylic acid copolymer, straight silicone resins having organosiloxane bonds or modified resins thereof, fluoride resins, polyester, polyurethane, polycarbonate, phenol resins, amino resins, melamine resins, benzoguanamine resins, urea resins, amide resins, epoxy resins and the like.

The volume average particle size of a carrier is preferably $45\text{ }\mu\text{m}$ or less, more preferably 10 to $40\text{ }\mu\text{m}$ or less. A volume average particle size of a carrier of $45\text{ }\mu\text{m}$ or less serves to prevent the soiled background and the uneven density as a result of retarded charging, poor charge distribution and reduced charge which are due to reduction in the particle size of the toner.

The weight ratio of a toner for developing an electrostatic latent image and a carrier to be mixed is, for example, preferably 1:100 to 20:100, more preferably 2:100 to 15:100, particularly 3:100 to 10:100.

Image forming method

A toner for developing an electrostatic latent image according to the present invention is used preferably in a method for forming an image comprising at least a latent image forming step in which an electrostatic latent image is formed on a latent image support, a toner layer forming step in which a toner layer is formed on the surface of a developer support which is located opposite, i.e., which faces, the electrostatic latent image support, a developing step in which the electrostatic latent image on the electrostatic latent image support is developed with the toner layer, and a transfer step in which a toner image developed is transferred onto a transfer material. The developing and transfer steps may be conducted using any conventional, well known methods.

By using a toner for developing an electrostatic latent image according to the present invention, an image exhibiting satisfactory minute line reproducibility and gradation without fogging can be obtained. Such satisfactory minute line reproducibility is extremely advantageous especially when developing a digital latent image.

Also in a method for forming a full color image by overlaying sequentially in any order the toner images of at least three colors including cyan, magenta and yellow onto the transfer material, or of four colors further including black, the use as each of these three or four color toners as

toners for developing an electrostatic latent image according to the present invention enables the formation of an image which exhibits satisfactory minute line reproducibility and gradation and undergoes no fogging and which is visually natural and equivalent in its quality to an image obtained by an offset printing as a result of the reduced toner image thickness on a transfer material attributable to the small particle size of the toner. Because of such reduced toner image thickness on the transfer material, the image is less uneven and less irregular, and thus less damaged externally, thereby achieving a higher durability of the image once formed.

If a decrease of image thickness on a transfer material is attained by the above-mentioned decrease of toner size, a satisfactory image may not be easily obtained if a surface state of a transfer material is not appropriate as described above. Thus in the present invention, the method for forming images comprises a developing step in which a toner layer is formed on the surface of a developer support arranged opposed to a latent image support and an electrostatic latent image is developed on the latent image support by the toner layer, and a transfer step in which the toner image formed is transferred onto the transfer material. The above problems are avoided by making the ten point average surface roughness R_z on at least an image forming region of a transfer material $10\text{ }\mu\text{m}$ or less by using the above-mentioned small-sized toner. By using a transfer material having equal to or higher than a predetermined surface smoothness or more, a sufficient coloring property and image uniformity can thus be obtained, and a toner weight per unit area of a toner image on a transfer material can be decreased by using a small-sized toner. Also, an image glossiness is made uniform, namely, a uniform image glossiness corresponding to the surface glossiness of a transfer material itself is obtained, and minute line reproducibility and gradation can be made satisfactory, and image quality equal to or higher than an image formed by offset printing can be achieved.

The toner weight of the toner image transferred on the transfer material in the transfer step is preferably to be as low as possible so as to obtain a uniform image glossiness corresponding to the surface glossiness of the transfer material itself. More particularly, the toner weight of the toner image is preferably 0.40 mg/cm^2 or less, more preferably 0.35 mg/cm^2 or less, most preferably 0.30 mg/cm^2 or less.

A transfer material which has a smooth surface state at a point when provided for the transfer step may be suitably used. It is thus also effective to provide a surface-smoothing step by which a transfer material surface is smoothed before it is provided for a transfer step. With the image forming method having the surface-smoothing step in this way, the minute line reproducibility and gradation yielded are satisfactory and image quality equal to or higher than an image formed by offset printing can be attained even if a transfer material having a rough surface state is used.

The surface-smoothing step can attain the surface-smoothing purpose easily by forming a layer comprising a non-color transparent toner or a white toner on at least an image forming region of the transfer material. When the non-color transparent toner is used, a high image quality image can be obtained while making the best use of a color of the transfer material itself. On the other hand, when a white toner is used, a sufficient whiteness degree is given to the transfer material and a high image quality image can be obtained even if the whiteness degree of a transfer material is not sufficient.

Any non-color transparent toner or white toner can be used provided that an intended surface state of a transfer

material can be obtained. Such toners preferably have a volume average particle size of 2 to 10 μm .

The method for forming images of the present invention is further detailed below.

Developing step

The developing step of this still further aspect of the present invention is a step in which a toner layer is formed on the surface of a developer support arranged opposed to a latent image support, and an electrostatic latent image is subsequently developed by the toner layer.

In the developing step, the electrostatic latent image formed on the surface of the latent image support by any known method is developed by an electrically charged toner.

In an image forming method using a two-component developer system, a developer support is arranged opposed to a latent image support. A toner layer is formed on the surface of the developer support. The toner layer is preferably formed by the so called magnetic brush which is obtained by forming magnetic carrier on the surface of a developer support like a brush and attaching a toner to it, although other suitable methods may also be used. The toner layer enables toner to be electrostatically provided to the surface of the latent image support.

Toner

The toner used in this still further aspect of the present invention (color toner forming a toner image in the developing step) is the toner of one or more of the aspects of the invention.

Transfer step

The transfer step in this still further aspect of the present invention is a step in which a toner image formed on the surface of a latent image support is transferred onto a transfer material.

The ten point average surface roughness R_z of at least an image forming region of the transfer material provided for the transfer step is 10 μm or less in the present invention. Namely, the color toner of the present invention is extremely small-sized and a decrease of the image thickness on a transfer material can be attained, but a transfer material having a ten point average surface roughness R_z of at least an image forming region of 10 μm or less is required to be used in order to make use of the decreasing effect of the image thickness at maximum and to form an image having a high image quality equal to or more than an image formed by offset printing.

By smoothing the surface state of a transfer material provided for a transfer step to a certain extent, a sufficient image glossiness may be obtained, and by using a small-sized toner, a toner weight on the transfer material is decreased, image glossiness is made uniform, i.e., a uniform image glossiness corresponding to the surface glossiness of the transfer material itself is obtained and the minute line reproducibility and the gradation are improved. Thus, this still further aspect of the present invention achieves an image having a high image quality equal to or higher than an image obtained by offset printing.

The ten point average surface roughness R_z of the transfer material is preferably determined according to the determination method described in JIS B 0601, published Feb. 1, 1994 (1997 edition), incorporated herein by reference. Generally it can be determined easily by using a commercially available feeler type surface smoothness determining device. The reason why the ten point average surface roughness R_z as an index of a surface roughness is used in the present invention, is as follows.

When a small-sized toner as the color toner of any of the aspects of the present invention is used, there may be a

problem that if the smoothness of the surface of the transfer material is not sufficient, for example, it is highly uneven, the color toner transferred onto the transfer material may be buried in concave parts of the transfer material. For example, if the transfer material is paper, the color toner may be buried between fibers of the paper. Also, the color toner may not easily be made completely molten in the transfer step, and the color reproduced area is limited. The problem with respect to the burying of the color toner in the concave parts is associated with the actual depth of the concave parts of the surface of the transfer material. Thus, the ten point average surface roughness R_z , which can show a depth of minute concave parts of the surface of the transfer material sufficiently, is considered to be suitable as an index of the surface roughness of the transfer material.

In the present invention, the minute line reproducibility and the gradation of an image obtained can be improved by making the ten point surface roughness R_z of the surface of a transfer material of 10 μm or less with the use of a small-sized toner. The ten point average surface roughness R_z of the surface of a transfer material is preferably 10 μm or less, and is more preferably 5 μm or less.

The preferable lower limit of the ten point average surface roughness R_z is not specified since the surface of a transfer material is required to be more smooth, but the ten point average surface roughness R_z of the surface of a transfer material which is actually obtained from the view point of manufacture, is about 2 μm at a minimum.

The region on the surface of a transfer material which must be a surface state having a ten point average surface roughness R_z of 10 μm or less, is required to be a side on which an image is formed and to be at least an image forming region. The image forming region indicates an area other than an area on which an image is not formed such as the outer periphery of the transfer material. The entire of the side on which an image is formed and the side on which an image is not formed may have the ten point average surface roughness R_z of 15 μm or less.

More particularly, a transfer material may be made to have a ten point average surface roughness R_z of 10 μm or less by coating thereon a resin or a coating agent in which a white pigment is dispersed in a binder resin. For example, a paper for use in electrophotography and the like having a ten point average surface roughness R_z of about 16 to 35 μm may be used once coated with such a coating to reduce the surface roughness R_z .

Additional examples of suitable transfer materials include a so called synthetic paper having a ten point average surface roughness R_z of 10 μm or less such as a paper for printing such as cast coated paper, art paper, machine coated paper obtained by coating to a high-quality paper used in a printing such as offset printing, photogravure, a transfer material which is made as a film by dispersing a white pigment in a thermoplastic resin such as polyester, polypropylene, a transfer material which is made as a film by applying whiteness degree equal to paper by making minute space in a thermoplastic resin, or a transfer material which is coated by a coating agent in which a white pigment is dispersed in a binder resin to the surface of a film.

Surface-smoothing step

It is sufficient for a transfer material to have a smooth surface state when provided for the transfer step. Thus it is possible to include a surface-smoothing step by which a transfer material surface is smoothed before being provided for the transfer step. With the image forming method having the surface-smoothing process in this way, even if a transfer material having a rough surface state is used, minute line

reproducibility and gradation are made satisfactory and an image quality equal to or higher than an image formed by offset printing can be achieved.

The surface state of the transfer material after being smoothed as in the surface-smoothing step, the surface preferably has a ten point average surface roughness Rz of 10 μm or less, more preferably 5 μm or less.

The surface-smoothing step can attain the purpose of the surface smoothing easily by making it a step in which a layer comprising a non-color transparent toner or a white toner is formed on at least an image forming region on the surface of the side of a transfer material on which an image is to be formed.

To further explain the method, in addition to three or four developing devices filled with each developer comprising each color toner of cyan, magenta and yellow and further black if necessary, a developing device filled with a developer comprising a non-color transparent toner or a white toner (which is referred as "surface-smoothing developing device" hereinafter) may be provided. A transfer material is surface-smoothed by developing and transferring the non-color transparent toner or the white toner on an image region formed on the transfer material with a color toner or the entire surface of the transfer material in a sufficient amount to smooth the surface. Preferably, the amount is sufficient to have a ten point average surface roughness Rz of 10 μm or less. The transfer material is then provided for the next transfer step of color toner.

On the transfer material which has been surface-smoothed, a toner image with a color toner is transferred and fixed to form an image. As described, the explanation is made by way of the example in which a full-color image is formed on a transfer material, but to include a surface smoothing step is also preferable from the view point of the improvement of the minute line reproducibility and the gradation even when an image of single color such as black is formed.

To form a toner image with a color toner without fixing after forming a non-color transparent toner layer or a white toner layer on a transfer material, is preferable in view of minimization and simplification of a device and further of a decrease of power consumption. The non-color transparent toner layer or a white toner layer is heated and fixed with a fixing roll and the like in a fixing step of a toner image with a color toner, and by embedding the concave parts of the surface of a transfer material having a ten point average surface roughness Rz exceeding 10 μm with such surface smoothing material, the embedding into the concave parts of a color toner can be effectively prevented.

The ten point average surface roughness Rz of the surface of a transfer material on which a non-color transparent toner layer or a white toner layer is formed can be determined by forming only a non-color transparent toner layer or a white toner layer, and determining as to the surface of the transfer material on which it is fixed. If a non-color transparent toner layer or a white toner layer is fixed before providing for a fixing step of a toner image with a color toner, the purpose of smoothing of the surface of a transfer material can be attained sufficiently.

When a non-color transparent toner is applied in the surface-smoothing step, a high image quality can be obtained while making the best use of the color of the transfer material. On the other hand, when a white toner is applied, even if the whiteness degree of the transfer material is not sufficient, a sufficient whiteness degree is provided to the transfer material, and thus a high image quality image can be obtained. Whether a non-color transparent toner or a

white toner is used in the surface-smoothing step, one can select appropriately based on the original whiteness degree of the transfer material used and the whiteness degree to be obtained.

The whiteness degree for a transfer material is preferably 70% or higher, more preferably 80% or more from the view point of color reproducibility in the case when the image formed is full-color. Therefore, when the original whiteness degree of the transfer material used is less than 70%, it is desirable to increase it to 70% or higher, more preferably 80% or more, by using a white toner.

The term whiteness degree means a value determined by the Hunter whiteness degree test method for paper and pulp according to JIS P 8123, published Sep. 1, 1994 (1996 edition), incorporated herein by reference.

The non-color transparent toner and the white toner applicable to the surface-smoothing step will now be described.

The non-color transparent toner and the white toner comprise at least a binding resin such as in the color toner, and in the case of the white toner, it further contains a white colorant.

As the binding resin constituting the non-color transparent toner and the white toner, the same materials as explained above for the color toner according to the present invention may suitably be used. In addition, the glass transition point and the softening point, etc., of the binding resin are the same as that explained for the color toner according to the present invention.

As the white colorant used in the white toner, an inorganic pigment such as titanium oxide, zinc oxide, zinc sulfate, antimony oxide, zirconium oxide having a particle size in the range from 0.05 to 0.5 μm may, for example, be used. From the view point of the whiteness degree and hiding power, titanium oxide is preferable.

To the non-color transparent toner and the white toner, a non-color or pale color charge-controlling agent may be added. As the charge-controlling agent, a basic electron donative compound such as a quaternary ammonium salt or benzoguanamine for a positive charging toner, and an electron suction compound such as salicylate metal salt, organic boron compound for a negative charging toner, may be used. If added, the amount of the charging controlling agent to be added is preferably in the range of, for example, 2 to 10% by weight to the binder resin provided that the amount does not affect the color reproducibility and transparency of an image obtained by the image forming method of the present invention (in particular full-color image), the non-color property and transparency in the case of the non-color transparent toner, and the whiteness degree in the case of the white toner.

A releasing agent such as wax may also be added to the non-color transparent toner and the white toner in order to prevent hot offset in a fixing step. As a releasing agent which may be used, for example, a low molecular weight polyethylene, a low molecular weight polypropylene, an aliphatic hydrocarbon wax such as microcrystalline wax, paraffin wax, an aliphatic wax such as camauba wax, montan wax and the like can be exemplified. If added, the amount of the releasing agent to be added is preferably in the range of, for example, 0.1 to 20% by weight, more preferably in the range from 2 to 10% by weight to the binder resin, provided that the amount does not affect the color reproducibility and transparency of an image obtained by the image forming method of the present invention (in particular full-color image), the non-color property and transparency in the case of the non-color transparent toner, and the whiteness degree in the case of the white toner.

The volume average particle size of the non-color transparent toner and the white toner, and the thickness of the layer of the non-color transparent toner or the white toner formed in the surface-smoothing step, may be controlled appropriately respectively so as to preferably yield a ten point average surface roughness R_z of the transfer material of 10 μm . For example, when a transfer material having a relatively high surface-smoothing property (namely, the ten point average surface roughness R_z is near 10 μm), it is sufficient to form a relatively thin layer of a non-color transparent toner or a white toner by laying a relatively small-sized non-color transparent toner or white toner on a transfer material in a relatively small amount. On the other hand, when a transfer material having a relatively low surface-smoothing property (namely, the ten point average surface roughness R_z greatly exceeds 10 μm), the ten point average surface roughness R_z may be made 10 μm or less by forming a relatively thick layer of a non-color transparent toner or a white toner by laying a relatively large-sized non-color transparent toner or white toner on a transfer material in a relatively large amount.

For example, an appropriate volume average particle size of the non-color transparent toner and the white toner is preferably in the range from 2 to 10 μm , more preferably in the range from 3 to 7 μm , most preferably in the range from 2 to 5 μm , which can be determined appropriately in line with the surface state of the transfer material as described above.

In addition, the weight of the non-color transparent toner or the white toner on the surface of the transfer material, can also be determined appropriately in line with the surface state of the transfer material as described above. However, a certain degree of amount is required to the surface-smoothing, and on the other hand, an amount as low as possible is preferable in the view point of the curl of a transfer material. Thus, the amount of the non-color transparent toner or a white toner on the surface of a transfer material is preferably in the range of, for example, 0.10 to 0.50 mg/cm^2 , more preferably in the range from 0.20 to 0.40 mg/cm^2 .

The surface smoothing step is preferably carried out by a method using the above non-color transparent toner or a white toner because it is easy, but the step can also be carried out by any other suitable methods. As the other methods, methods for coating a coating material such as resin which can smooth the surface of a transfer material by known coating methods such as roll coating method or blade coating method may be mentioned.

As a resin which can smooth the surface of the transfer material, a thermoplastic resin and the like such as polyester, styrene-(meth)acrylic acid ester copolymer, styrene-butadiene copolymer, etc., may be exemplified.

EXAMPLES

The present invention is further described in the following examples. While all of the toners for developing electrostatic latent images produced in the examples are negatively charged toners, it is a matter of course that positively charged toners are similar to the negatively charged toners except for inverted polarity.

Experiment 1

Examples 1-15 and Comparative Examples 1-12

(1) Preparation of flushing pigment

Magenta flushing pigment

70 parts by weight of polyester resin (bisphenol-A type polyester: bisphenol A ethylene oxide adduct-cyclohexane

dimethanol-terephthalic acid, weight average molecular weight: 11,000, number average molecular weight: 3,500, T_g : 65° C.) and 75 parts by weight of a magenta pigment (C.I. Pigment Red 57:1) hydrated paste (pigment: 40% by weight) are placed in a kneader and mixed, and heated gradually. Kneading is continued at 120° C., and, after allowing separation of the aqueous layer and the resin layer, water is removed and the resin layer is further kneaded to remove water, and dehydrated to obtain a magenta flushing pigment.

Cyan flushing pigment

A cyan flushing pigment is obtained in the same manner as the magenta flushing pigment except for using a cyan pigment (C.I. Pigment Blue 15:3) hydrated paste (pigment: 40% by weight) instead of the magenta pigment hydrated paste.

Yellow flushing pigment

A yellow flushing pigment is obtained in the same manner as the magenta flushing pigment except for using a yellow pigment (C.I. Pigment Yellow 17) hydrated paste (pigment: 40% by weight) instead of the magenta pigment hydrated paste.

(2) Coloring particle preparation

Preparation 1 of coloring particle

Polyester resin (bisphenol-A type polyester: bisphenol A ethylene oxide adduct-cyclohexane dimethanol/terephthalic acid, weight average molecular weight: 11,000, number average molecular weight: 3,500, T_g : 65° C.)

66.7 parts by weight

The above magenta flushing pigment (pigment: 30% by weight)

33.3 parts by weight

The above components are melted and kneaded with a Banbury mixer, cooled, finely ground with a jet mill, and classified with an air-classifier to obtain coloring particles A, B, J, T, and U having each particle size distribution shown in Table 1 by varying conditions of grinding and classification.

The particle size and the particle size distribution of particles are determined using a Coulter counter model TA II manufactured by Coulter Co., Ltd. In this determination, a 100 μm aperture tube is used for a toner (coloring particle) having an average particle size exceeding 5 μm , and a toner having an average particle size 5 μm or less is determined at the aperture size of 50 μm , and the frequency distribution of the particle having a size of 1 μm or less is determined at the aperture size of 30 μm . (Particle size is determined similarly in the following Examples and Comparatives Examples.)

Preparation 2 of coloring particle

A coloring particle D shown in Table 1 is obtained in the same manner as Preparation 1 of coloring particle except for using cyan flushing pigment instead of magenta flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 3 of coloring particle

A coloring particle E shown in Table 1 is obtained in the same manner as Preparation 1 of coloring particle except for using 50 parts by weight of polyester resin and 50 parts by weight of yellow flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 4 of coloring particle

A coloring particle C shown in Table 1 is obtained in the same manner as Preparation 1 of coloring particle except for

using 90 parts by weight of polyester resin and 10 parts by weight of carbon black (primary particles average diameter 40 nm). The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 5 of coloring particle

A coloring particle F shown in Table 1 is obtained in the same manner as Preparation 1 of coloring particle except for using 73.3 parts by weight of polyester resin and 26.7 parts by weight of magenta flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 6 of coloring particle

A coloring particle K shown in Table 1 is obtained in the same manner as described in Preparation 1 of coloring particle except for using 83.4 parts by weight of polyester resin and 16.6 parts by weight of magenta flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 7 of coloring particle

A coloring particle L shown in Table 1 is obtained in the same manner as described in Preparation 1 of coloring particle except for using 80 parts by weight of polyester resin and 20 parts by weight of magenta flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 8 of coloring particle

A coloring particle P shown in Table 1 is obtained in the same manner as described in Preparation 1 of coloring particle except for using 86.7 parts by weight of polyester resin and 13.3 parts by weight of magenta flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 9 of coloring particle

A coloring particle H shown in Table 1 is obtained in the same manner as described in Preparation 2 of coloring particle except for using 73.3 parts by weight of polyester resin and 26.7 parts by weight of cyan flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 10 of coloring particle

A coloring particle N shown in Table 1 is obtained in the same manner as described in Preparation 2 of coloring particle except for using 80 parts by weight of polyester resin and 20 parts by weight of cyan flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 11 of coloring particle

A coloring particle R shown in Table 1 is obtained in the same manner as described in Preparation 2 of coloring particle except for using 86.7 parts by weight of polyester resin and 13.3 parts by weight of cyan flushing pigment. The

conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 12 of coloring particle

A coloring particle I shown in Table 1 is obtained in the same manner as described in Preparation 3 of coloring particle except for using 60 parts by weight of polyester resin and 40 parts by weight of yellow flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 13 of coloring particle

A coloring particle O shown in Table 1 is obtained in the same manner as described in Preparation 3 of coloring particle except for using 73.3 parts by weight of polyester resin and 26.7 parts by weight of yellow flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 14 of coloring particle

A coloring particle S shown in Table 1 is obtained in the same manner as described in Preparation 3 of coloring particle except for using 83.3 parts by weight of polyester resin and 16.7 parts by weight of yellow flushing pigment. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 15 of coloring particle

A coloring particle G shown in Table 1 is obtained in the same manner as described in Preparation 4 of coloring particle except for using 93 parts by weight of polyester resin and 7 parts by weight of carbon black. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 16 of coloring particle

A coloring particle M shown in Table 1 is obtained in the same manner as described in Preparation 4 of coloring particle except for using 96 parts by weight of polyester resin and 4 parts by weight of carbon black. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

Preparation 17 of coloring particle

A coloring particle Q shown in Table 1 is obtained in the same manner as described in Preparation 4 of coloring particle except for using 97 parts by weight of polyester resin and 3 parts by weight of carbon black. The conditions of grinding and classification are adjusted to obtain a particle size distribution shown in Table 1.

In the following Table 1, pigment concentration C (%) in each coloring particle, true specific weight a of each coloring particle, aDC calculated from these values and volume average particle size D (μm) of the coloring particles, and average particle size of a dispersed particle in binder resin of pigment fine particle (circle diameter: μm) are described as well as the descriptions with regard to the particle size of the coloring particles A to U obtained above.

TABLE 1

Kinds of Coloring Particle	Volume Average Particle Size D (μm)	Particle Exceeding 5.0 μm (% by Number)	Particle of 4.0 μm or Less (% by Number)	Particle 1.0 μm or Less (% by Number)	Color of Colorant	Pigment Concentration C (%)	True Specific Gravity a	a D C ($a \times D \times C$)	Size of Dispersed Pigment (μm)*2	Particle of 1.0 to 2.5 μm (% by Number)
Coloring Particle A	3.0	0.5	93.2	8.0	M	10	1.24	37.2	0.25	44.1
Coloring Particle B	3.6	2.2	89.6	3.0	M	10	1.24	44.6	0.20	36.5
Coloring Particle C	3.5	2.0	88.0	3.0	K	10	1.20	42.0	—	41.2

TABLE 1-continued

Kinds of Coloring Particle	Volume Average Particle Size D (μm)	Particle Exceeding 5.0 μm (% by Number)	Particle of 4.0 μm or Less (% by Number)	Particle 1.0 μm or Less (% by Number)	Color of Colorant	Pigment Concentration C (%)	True Specific Gravity a	a D C (a \times D \times C)	Size of Dispersed Pigment (μm) ²	Particle of 1.0 to 2.5 μm (% by Number)
Coloring Particle D	3.6	1.6	90.8	2.9	C	10	1.24	44.6	0.23	35.1
Coloring Particle E	3.6	1.7	90.6	2.9	Y	15	1.25	67.5	0.20	37.3
Coloring Particle F	3.5	2.4	89.5	3.1	M	8	1.23	34.4	0.18	36.4
Coloring Particle G	3.4	2.0	90.9	3.3	K	7	1.20	28.6	—	37.2
Coloring Particle H	3.3	1.8	92.0	3.6	C	8	1.23	32.5	0.19	40.5
Coloring Particle I	3.6	2.6	88.4	3.0	Y	12	1.25	54.0	0.18	38.2
Coloring Particle J	4.2	8.1	77.2	2.0	M	10	1.24	52.1	0.20	32.1
Coloring Particle K	3.6	2.1	87.0	3.1	M	5	1.22	22.0	0.23	39.2
Coloring Particle L	5.7	28.4	39.2	0.0	M	6	1.22	41.7	0.25	6.2
Coloring Particle M	6.1	35.6	37.0	1.8	K	4	1.20	29.3	—	6.0
Coloring Particle N	5.8	30.6	39.0	2.1	C	6	1.22	42.5	0.21	5.8
Coloring Particle O	5.9	33.4	38.0	1.7	Y	8	1.22	57.6	0.20	6.1
Coloring Particle P	7.8	84.1	6.2	1.8	M	4	1.22	38.1	0.24	4.8
Coloring Particle Q	8.2	89.2	4.2	2.0	K	3	1.20	29.5	—	4.5
Coloring Particle R	7.5	80.1	7.8	2.3	C	4	1.22	36.6	0.21	5.6
Coloring Particle S	7.6	81.1	7.6	2.2	Y	5	1.21	46.0	0.24	5.2
Coloring Particle T	2.8	1.0	95.1	25.4	M	10	1.24	34.7	0.21	51.0
Coloring Particle U	4.4	12.1	72.5	2.1	M	10	1.24	54.6	0.26	44.1

Legend of colorants: K: black, M: magenta, C: cyan, Y: yellow

(3) Preparation of toner for developing an electrostatic latent image

To each of the above described coloring particles A to U, silica (SiO_2) fine particles whose surface has been imparted with hydrophobicity using hexamethyldisilazane (HMDS) and whose primary particle size is 40 nm, and metatitanic acid compound fine particles which are the reaction product of metatitanic acid and i-butyltrimethoxysilane and whose primary particle size is 20 nm, are added so as to have each coating rate to the surface of each coloring particle of 40%, and mixing with a Henschel mixer to yield toners for developing an electrostatic latent image A to U (each of the symbols A to U appended to the obtained each toner for developing an electrostatic latent image is corresponding to each of the symbol A to U of the used coloring particle).

The coating rate to the surface of the coloring particle used herein is the value F(%) determined by the above described Formula (2).

Carrier Preparation

100 Parts by weight of a Cu—Zn ferrite fine particles having a volume average particle size of 40 μm is admixed with a methanol solution containing 0.1 parts by weight of γ -aminopropyl-triethoxysilane, and coating is effected using a kneader, and then the silane compound is hardened completely by distilling methanol off followed by heating for 2 hours at 120° C. The particle thus obtained is admixed with perfluorooctylethyl methacrylate-methyl methacrylate copolymer (copolymerization ratio, 40:60 by weight) dis-

solved in toluene and subjected to a vacuum kneader to yield a resin-coated carrier having 0.5% by weight of the perfluorooctylethyl methacrylate-methyl methacrylate copolymer as a coating thereon, to yield a resin-coated type carrier used in the following Examples and Comparative Examples.

Example 1

The resin-coated type carrier; 100 parts by weight is admixed with Toner A; 4 parts by weight using a V type mixer to obtain a two-component developer of Example 1.

Example 2

A two-component developer of Example 2 is obtained in the same manner as described in Example 1 except for using Toner B; 4 parts by weight instead of Toner A; 4 parts by weight.

Example 3

A two-component developer of Example 3 is obtained in the same manner as described in Example 1 except for using Toner C; 4 parts by weight instead of Toner A; 4 parts by weight.

Example 4

A two-component developer of Example 4 is obtained in the same manner as described in Example 1 except for using Toner D; 4 parts by weight instead of Toner A; 4 parts by weight.

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Example 5

A two-component developer of Example 5 is obtained in the same manner as described in Example 1 except for using Toner E; 4 parts by weight instead of Toner A; 4 parts by weight.

Example 6

A two-component developer of Example 6 is obtained in the same manner as described in Example 1 except for using Toner F; 5 parts by weight instead of Toner A; 4 parts by weight.

Example 7

A two-component developer of Example 7 is obtained in the same manner as described in Example 1 except for using Toner G; 5 parts by weight instead of Toner A; 4 parts by weight.

Example 8

A two-component developer of Example 8 is obtained in the same manner as described in Example 1 except for using Toner H; 5 parts by weight instead of Toner A; 4 parts by weight.

Example 9

A two-component developer of Example 9 is obtained in the same manner as described in Example 1 except for using Toner I; 5 parts by weight instead of Toner A; 4 parts by weight.

Example 10

A two-component developer of Example 10 is obtained in the same manner as described in Example 1 except for using Toner J; 6 parts by weight instead of Toner A; 4 parts by weight.

Example 11

A two-component developer of Example 11 is obtained in the same manner as described in Example 1 except for using Toner K; 5 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 1

A two-component developer of Comparative Example 1 is obtained in the same manner as described in Example 1 except for using Toner L; 5 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 2

A two-component developer of Comparative Example 2 is obtained in the same manner as described in Example 1 except for using Toner M; 5 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 3

A two-component developer of Comparative Example 3 is obtained in the same manner as described in Example 1 except for using Toner N; 5 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 4

A two-component developer of Comparative Example 4 is obtained in the same manner as described in Example 1

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except for using Toner O; 5 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 5

A two-component developer of Comparative Example 5 is obtained in the same manner as described in Example 1 except for using Toner P; 6 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 6

A two-component developer of Comparative Example 6 is obtained in the same manner as described in Example 1 except for using Toner Q; 6 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 7

A two-component developer of Comparative Example 7 is obtained in the same manner as described in Example 1 except for using Toner R; 6 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 8

A two-component developer of Comparative Example 8 is obtained in the same manner as described in Example 1 except for using Toner S; 6 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 9

A two-component developer of Comparative Example 9 is obtained in the same manner as described in Example 1 except for using Toner T; 4 parts by weight instead of Toner A; 4 parts by weight.

Comparative Example 10

A two-component developer of Comparative Example 10 is obtained in the same manner as described in Example 1 except for using Toner U; 4 parts by weight instead of Toner A; 4 parts by weight.

Methods for various evaluations

Each two-component developer obtained in each of Examples 1 to 11 and Comparative Examples 1 to 10 is used to make the various evaluations as shown below.

In the following various evaluations, J coat paper manufactured by Fuji Xerox Co., Ltd. is employed as a transfer material, and a modified model of A color 935 manufactured by Fuji Xerox Co., Ltd. (modified to control the voltage upon development by means of external power source, hereinafter simply referred to as modified A color 935) is employed as an image forming device. The evaluations are all carried out under an environmental condition at a temperature of 22° C. and a humidity of 55%. The image formation is carried out appropriately with controlling image density in the range from 1.6 to 2.0.

TMA

A solid image having an area rate of 100% is formed, and the weight of toner per unit area of the image area (TMA: mg/cm²) is determined. As the method of the determination, an un-fixed solid image having an area rate of 100% is formed on a transfer material. It is weighed. The un-fixed toner on the transfer material is removed by air-blowing, then the weight of only the transfer material is determined. The TMA is calculated from the weight difference between before and after the removal of the un-fixed toner.

Image Density

A solid area having an area rate of 100% is formed, and the image density of the image area is determined using X-Rite404 (manufactured by X-Rite Co., Ltd.).

Minute Line Reproducibility Evaluation

Minute line image is formed so as to have a line width of 50 μm on a photosensitive body, and it is transferred on a transfer material and fixed. The minute line image of the fixed image on the transfer material is observed using a VH-6220 microhighscope (KEYENCE Co., Ltd.) with a 175 \times magnification. Evaluation is made with the criteria as shown below. The \odot and \circ are regarded as acceptable.

\odot : Minute lines are filled uniformly with toner and no disturbed edges are observed.

\circ : Minute lines are filled uniformly with toner but slightly jagged edges are observed.

Δ : Minute lines are filled almost uniformly with the toner but jagged edges are observed evidently.

\times : Minute lines are not filled uniformly with the toner. Jagged edges are observed very evidently.

Gradation Reproducibility Evaluation

A gradation image having an image area rate of 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or 100% is

visually and observed using a VH-6220 microhighscope (KEYENCE Co., Ltd.) with a 175 \times magnification, and the graininess on highlighted areas is evaluated. The criteria for evaluation are as follow. The \odot and \circ are regarded as acceptable.

\odot : The graininess for both 5% and 10% are very satisfactory.

\circ : The graininess for 5% is somewhat bad, but the graininess is generally satisfactory.

Δ : The graininess for 5% is bad.

\times : The graininess for both 5% and 10% are bad.

Cleanability

Cleanability is designated as \circ when no poor cleaning occurred during reproducing 3,000 copies, and as \times when poor cleaning occurred.

The results of the evaluations for each toner obtained in Examples 1 to 11 and Comparative Examples 1 to 10 are summarized in Table 2.

TABLE 2

Example/ Comparative Example	Developer			Particle Size of Carrier (μm)	TMA mg/cm ²	Image Density	Minute Line Reproducibility	Gradation	Graininess on Highlight Area	Cleanability
	Kinds of Toner	Color								
Example	1	A	M	40	0.25	1.8	\odot	\odot	\odot	\circ
	2	B	M	40	0.25	1.9	\odot	\odot	\odot	\circ
	3	C	K	40	0.25	1.8	\odot	\odot	\odot	\circ
	4	D	C	40	0.25	1.8	\odot	\odot	\odot	\circ
	5	E	Y	40	0.25	1.7	\odot	\odot	\odot	\circ
	6	F	M	40	0.35	1.8	\odot	\odot	\odot	\circ
	7	G	K	40	0.35	1.8	\odot	\odot	\odot	\circ
	8	H	C	40	0.35	1.7	\odot	\odot	\odot	\circ
	9	I	Y	40	0.35	1.6	\odot	\odot	\odot	\circ
	10	J	M	40	0.35	2.0	\circ	\circ	\circ	\circ
	11	K	M	40	0.45	1.8	\circ	\circ	\odot	\circ
Comparative Example	1	L	M	40	0.45	1.8	Δ	Δ	Δ	\circ
	2	M	K	40	0.45	1.8	Δ	Δ	Δ	\circ
	3	N	C	40	0.45	1.8	Δ	Δ	Δ	\circ
	4	O	Y	40	0.45	1.6	Δ	Δ	Δ	\circ
	5	P	M	40	0.65	1.8	\times	\times	\times	\circ
	6	Q	K	40	0.65	1.8	\times	\times	\times	\circ
	7	R	C	40	0.65	1.8	\times	\times	\times	\circ
	8	S	Y	40	0.65	1.6	\times	\times	\times	\circ
	9	T	M	40	0.25	1.8	\odot	\odot	\odot	\times
	10	U	M	40	0.25	1.8	Δ	Δ	Δ	\circ

made and examined for its image density using X-Rite model 404 (manufactured by X-Rite Co., Ltd.) to evaluate the gradation. The concrete criteria for evaluation are as follow. The \odot and \circ are regarded as acceptable.

\odot : From the low image area rate part to the high image area rate part, the gradation for all gradation images are very satisfactory.

\circ : From the low image area rate part to the high image area rate part, the gradation for all gradation images are satisfactory.

Δ : The gradation reproducible range is somewhat limited in the low image area part, and the gradation is somewhat unstable.

\times : The gradation reproducible range is limited in the high/low image area part, and the gradation is unstable.

Graininess On Highlight Area

Gradation images each having an image area rate of 5% and 10% are formed. The obtained image is observed

From the results, it can be seen that, with the toner for developing an electrostatic latent image of the present invention, an image having satisfactory minute line reproducibility, gradation reproducibility, and graininess on highlighted areas can be formed, and that satisfactory cleanability can be obtained. With Example 10, in which the coloring particle has a somewhat large volume average particle size, the minute line reproducibility, gradation reproducibility, and graininess on highlighted areas are somewhat lowered compared with the other Examples, but these are still in the acceptable range. In addition, with Example 11, in which the low pigment concentration has an aDC value of 25 or less, the image quality impression is somewhat inferior due to the high TMA of the toner, but the graininess on highlighted areas is excellent, and thus it is deemed to be satisfactorily favorable compared with the case where the conventional toner is used.

To the contrary, with Comparative Examples 1 to 8, in which the coloring particles have large volume average

particle size, and with Comparative Example 10, in which the amount of the coloring particles having a size exceeding $5\ \mu\text{m}$ is high (even though the volume average particle size of the coloring particles is controlled to a some extent), the cleanability is acceptable, but the minute line reproducibility, gradation reproducibility, and graininess on highlighted areas (which are the aims of the present invention) are low. Thus a satisfactory image could not be obtained. Further, with Comparative Example 9, the minute line reproducibility, gradation reproducibility, and graininess on highlighted areas are satisfactory, but cleanability is remarkably deteriorated. The reason for this is that, although the obtained image itself can be satisfactory because the volume average particle size of the coloring particles is small, the rate of the coloring particles having a size of $1.0\ \mu\text{m}$ or less is large, and it thus cannot be actually used.

Example 12

A full color copy test using three colors is carried out using each developer of magenta, cyan, and yellow obtained in Examples 2, 4, and 5. The copy test is made using a modified A color 935 as an image forming device under a condition of at a temperature of 22°C . and humidity of 55%. The evaluations of graininess on highlighted areas and image uniformity are made by generating a photographic image.

The evaluation items are as follows. The results are summarized in Table 3.

TMA

A solid image having an area rate of 100% using a single color for each of magenta, cyan, and yellow, and a black image having an area rate of 100% comprising magenta, cyan, and yellow are each formed, and the toner weight per unit area of the image area (TMA: mg/cm^2) is determined. The method for determination is the same as that for Examples 1 to 11.

Image Density

Solid areas each having an area rate of 100% with a single color for each of magenta, cyan, and yellow used, and a black image having an area rate of 100% comprising the three colors of magenta, cyan, and yellow are formed respectively, and the image density of each of the image areas is determined using X-Rite 404 (manufactured by X-Rite Co., Ltd.).

Graininess On Highlight Area

Gradation images having image areas of 5% and 10% standards are formed. The obtained images are observed visually, and the graininess on highlight areas is evaluated. The criteria for evaluation are as follow. The \odot and \circ are regarded as acceptable.

\odot : The graininess for both 5% and 10% are very satisfactory.

\circ : The graininess for 5% is somewhat bad, but the graininess is generally satisfactory.

Δ : The graininess for 5% is bad.

\times : The graininess for both 5% and 10% are bad.

Image Uniformity

As for the obtained photographic image, the degrees of the image uniformity due to the difference of irregularities between an imaged area and a non-imaged area and between a high density area and a low density area, are evaluated visually. The concrete evaluation criteria are as follows. The \circ is regarded as to be acceptable.

\circ : Uniformity is equivalent or higher to offset printing.

Δ : Uniformity is slightly lower than offset printing.

\times : Uniformity is markedly lower than offset printing.

Example 13

A full color copy test is made using three colors in the same manner as described in Example 12, using each developer of magenta, cyan, and yellow obtained in Examples 6, 8 and 9. The results are summarized in Table 3.

Example 14

A full color copy test is made using four colors in the same manner as described in Example 12, using each developer of magenta, cyan, yellow, and black obtained in Examples 2, 4, 5 and 3. For the TMA and image density, the test is made for the black single-color toner. The results are summarized in Table 3.

Example 15

A full color copy test is made using four colors in the same manner as described in Example 12, using each developer of magenta, cyan, yellow, and black obtained in Examples 6, 8, 9 and 7. For the TMA and image density, the test is made for the black single-color toner. The results are summarized in Table 3.

Comparative Example 11

A full color copy test is made using four colors in the same manner as described in Example 12, using each developer of magenta, cyan, yellow, and black obtained in Comparative Examples 1, 3, 4 and 2. For the TMA and image density, the test is made for the black single-color toner. The results are summarized in Table 3.

Comparative Example 12

A full color copy test is made using four colors in the same manner as described in Example 12, using each developer of magenta, cyan, yellow, and black obtained in Comparative Examples 5, 7, 8 and 6. For the TMA and image density, the test is made for black single-color toner. The results are summarized in Table 3.

TABLE 3

Developer										
Example - Comparative Example	12	Particle Size of Carrier (μm)	Kinds		Single Color		Process Black		Graininess on	
			of Toner	Color	TMA mg/cm^2	Image Density	TMA mg/cm^2	Image Density	Highlight Area	Image Uniformity
Ex.		40	B	M	0.25	1.9	0.75	1.8	⊙	⊙
			D	C	0.25	1.8				
			E	Y	0.25	1.7				

TABLE 3-continued

Example - Comparative Example	Developer			Single Color		Process Black		Graininess on	
	Particle Size of Carrier (μm)	Kinds of Toner	Color	TMA mg/cm ²	Image Density	TMA mg/cm ²	Image Density	Highlight Area	Image Uniformity
Comp. Ex.	13	40	C	K	0.25	1.8			
			F	M	0.35	1.8	1.04	1.8	○
			H	C	0.35	1.7			
			I	Y	0.35	1.6			
			G	K	0.35	1.8			
	11	40	L	M	0.45	1.8	1.34	1.8	Δ
			N	C	0.45	1.8			
			O	Y	0.45	1.6			
			M	K	0.45	1.8			
			P	M	0.65	1.8	1.95	1.8	X
	12	40	R	C	0.65	1.8			
			S	Y	0.65	1.6			
			Q	K	0.65	1.8			

From the above results, in Examples 12 to 15, in which full color images are obtained using the toner for developing an electrostatic latent image of the present invention, the TMA could be lowered even if three or four colors are overlaid. Further, a satisfactory full color image could be obtained which is excellent in graininess on highlight areas and has high image uniformity. In Examples 13 and 15, the pigment concentration is somewhat low and the TMA is somewhat high so as to satisfy the image density. Thus, the image thickness is somewhat large and both of the graininess on highlight parts and image uniformity are lowered compared with Examples 12 and 14. However, both are in the acceptable range and sufficiently satisfactory compared with the case where conventional toners are used.

To the contrary, with Comparative Examples 11 and 12, in which the coloring particles have a large volume average particle size, no problems with stability against the environment, powder flowability, and fogging are seen. However, the minute line reproducibility, gradation reproducibility, and image uniformity are low, and satisfactory image is not obtained.

Experiment 2

Examples 16 to 24 and Comparative Examples 13 to 19

Carrier preparation 1

100 parts by weight of a Cu—Zn ferrite microparticle having the volume average particle size of 40 μm is admixed with a methanol solution of 0.1 parts by weight of γ -aminopropyltriethoxysilane and coating is effected using a kneader, and then the silane compound is hardened completely by distilling methanol off followed by heating for 2 hours at 120° C. The particle thus obtained is admixed with perfluorooctylethyl methacrylate-methyl methacrylate copolymer (copolymerization ratio, 40:60 by weight) dissolved in toluene and subjected to a vacuum kneader to yield a resin-coated carrier having 0.5% by weight of the perfluorooctylethyl methacrylate-methyl methacrylate copolymer as a coating thereon.

Example 16

(1) Coloring particle preparation

Polyester resin A 90 parts by weight

Carbon black (primary average particle size: 40 nm) 10 parts by weight

The components shown above are mixed and kneaded, and the molten material is cooled, milled and classified to

obtain black coloring particles having the volume average particle size of 3.5 μm containing 2.0% by number of the particles having a particle size of 5.0 μm or more, 88% by number of the particles having a particle size of 4.0 μm or less, and 3% by number of the particles having a particle size of 1.0 μm or less.

Polyester A described above is a bisphenol-A ethylene oxide adduct/cyclohexane dimethanol/terephthalic acid (molecular weight Mw=11,000, Mn=3,500, glass transition point=65° C., softening point=105° C.).

The particle size and the particle size distribution are determined using a Coulter counter model TA II manufactured by Coulter Co., Ltd. In this determination, a 100 μm aperture tube is used for a toner (coloring particle) having an average particle size exceeding 5 μm and a toner having an average particle size less than 5 μm is determined at the aperture size of 50 μm , and the frequency distribution of the particle having a size of 1 μm or less is determined at the aperture size of 30 μm . Particle size is determined similarly in the following examples and comparative examples.

(2) Preparation of developer for electrostatic latent image

100 parts by weight of the black coloring particles obtained are mixed with 1.9 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using hexamethyldisilazane (HMDS) and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 25%) and 1.6 parts by weight of metatitanic acid compound microparticles which are the reaction product between metatitanic acid and i-butyltrimethoxysilane and whose primary particle size is 20 nm (true specific gravity: 3.2, coating rate based on the surface of the coloring particle: 30%) in a Henschel mixer to yield a black toner.

Metatitanic acid and i-butyltrimethoxysilane are reacted as described below. Thus, metatitanic acid slurry is admixed with 4 N aqueous solution of sodium hydroxide, adjusted at pH 9.0, stirred and then neutralized with 6 N hydrochloric acid. The mixture is filtered and the filter cake is washed and combined again with water to form a slurry, which is adjusted at pH 1.2 with 6 N hydrochloric acid, stirred for a certain period to effect peptization. The peptized slurry thus obtained is combined with i-butyltrimethoxysilane, stirred for a certain period, and then neutralized with 8 N aqueous solution of sodium hydroxide. The mixture is filtered and the filter cake is washed with water, dried at 150° C., milled using a jet mill, separated from coarse particles, thereby

obtaining metatitanic acid compound microparticles which is the reaction product between metatitanic acid and i-butytrimethoxysilane and whose primary particle size is 20 nm.

When the black toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.342 and the bottom value is -0.153. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity (30° C., 85% humidity also in the following description) and at a low temperature and a low humidity (10° C., 15% humidity also in the following description), the peak value and the bottom value at the high temperature and the high humidity are -0.324 and -0.144, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.360 and -0.171, respectively.

(3) Preparation of developer for electrostatic latent image
4 parts by weight of the black toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a black two-component developer.

Using this two-component developer, the evaluations summarized below are made.

Example 17

(1) Preparation of magenta flushing pigment

70 parts by weight of polyester resin A and 75 parts by weight of a magenta pigment (C.I. Pigment Red 57:1) hydrated paste (% pigment, 40% by weight) are placed in a kneader and mixed with heating gently. Kneading is continued at 120° C., and, after allowing to separate the aqueous layer from the resin layer, water is removed and the resin layer is further kneaded to remove water, dehydrated to obtain a magenta flushing pigment.

(2) Preparation of coloring particle

Polyester resin A 70 parts by weight

Magenta flushing pigment obtained above 30 parts by weight
(% pigment: 30% by weight)

Polyester resin A and the magenta flushing pigment shown above are mixed and kneaded, and the molten material is cooled, milled and classified to obtain magenta coloring particles.

A part of the magenta coloring particles are taken and observed by a transmission electron microscope at the magnification of 15,000 to take a photograph, which is then subject to evaluation by an image analyzer, which reveals that the pigment average disperse size of the coloring particles in the binder resin is 0.18 μ m as a circle diameter. Utilizing the Coulter counter model TA II, it is determined that the volume average particle size of the coloring particles are 3.0 μ m, the particles having a size of 5.0 μ m or more are present in the amount of 0.7% by number, the particles having a size of 4.0 μ m or less are present in the amount of 92% by number, and the particles having a size of 1.0 μ m or less are present in the amount of 5% by number.

(3) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particles, 3.0 parts by weight of silica (SiO₂) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 35%) and 2.5 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 40%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.351 and the bottom value is -0.144. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.324 and -0.135, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.378 and -0.153, respectively.

(4) Preparation of developer for electrostatic latent image
4 parts by weight of the magenta toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Example 18

(1) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particles obtained in Example 17, 2.6 parts by weight of silica (SiO₂) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 30%) and 2.5 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 40%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.315 and the bottom value is -0.153. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.297 and -0.144, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.324 and -0.163, respectively.

(2) Preparation of developer for electrostatic latent image

4 parts by weight of the magenta toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Example 19

(1) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particle obtained in Example 17, 3.9 parts by weight of silica (SiO₂) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 45%) and 1.9 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.414 and the

bottom value is -0.135. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.378 and -0.128, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.459 and -0.144, respectively.

(2) Preparation of developer for electrostatic latent image

4 parts by weight of the magenta toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Example 20

(1) Preparation of cyan flushing pigment

A cyan flushing pigment is obtained in the manner similar to that in Example 17 except for using a cyan pigment (C.I. Pigment Blue 15:3) hydrated paste (% pigment, 40% by weight) instead of the magenta pigment (C.I. Pigment Red 57:1) hydrated paste employed in the preparation of the magenta flushing pigment in Example 17.

(2) Preparation of coloring particle

Cyan coloring particles are obtained in the manner similar to that in Example 17 except for using the cyan flushing particle obtained above instead of the magenta flushing pigment employed in the preparation of the magenta coloring pigment in Example 17.

A part of the cyan coloring particles are taken and observed by a transmission electron microscope at the magnification of 15,000 to take a photograph, which is then subject to evaluation by an image analyzer, reveals that the pigment average disperse size of the coloring particles in the binder resin is 0.1 μm as a circle diameter. Analysis with the Coulter counter model TA II reveals that the volume average particle size of the coloring particles is 3.2 μm , the particles having a size of 5.0 μm or more are present in the amount of 0.9% by number, the particles having a size of 4.0 μm or less are present in the amount of 90% by number, and the particles having a size of 1.0 μm or less are present in the amount of 6% by number.

(3) Preparation of toner for developing electric latent image

100 parts by weight of the cyan coloring particles, 2.9 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 35%) and 2.4 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 40%) are mixed in a Henschel mixer to prepare a cyan toner.

When the cyan toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.405 and the bottom value is -0.144. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.378 and -0.135, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.432 and -0.162, respectively.

(4) Preparation of developer for electrostatic latent image

4 parts by weight of the cyan toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Example 21

(1) Preparation of yellow flushing pigment

A yellow flushing pigment is obtained in the manner similar to that in Example 17 except for using an yellow pigment (C.I. Pigment Yellow 17) hydrated paste (% pigment, 40% by weight) instead of the magenta pigment (C.I. Pigment Red 57:1) hydrated paste employed in the preparation of the magenta flushing pigment in Example 17.

(2) Preparation of coloring particle

Yellow coloring particles are obtained in the manner similar to that in Example 17 except for using the yellow flushing particle obtained above instead of the magenta flushing pigment employed in the preparation of the magenta coloring pigment in Example 17.

A part of the yellow coloring particles are taken and observed by a transmission electron microscope at the magnification of 15,000 to take a photograph, which is then subject to evaluation by an image analyzer, reveals that the pigment average disperse size of the coloring particles in the binder resin is 0.2 μm as a circle diameter. Analysis with the Coulter counter model TA II reveals that the volume average particle size of the coloring particles is 3.5 μm , the particles having a size of 5.0 μm or more are present in the amount of 2.2% by number, the particles having a size of 4.0 μm or less are present in the amount of 88% by number, and the particles having a size of 1.0 μm or less are present in the amount of 8% by number.

(3) Preparation of toner for developing electric latent image

100 parts by weight of the yellow coloring particles, 2.6 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 35%) and 2.2 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 40%) are mixed in a Henschel mixer to prepare an yellow toner.

When the yellow toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.369 and the bottom value is -0.162. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.351 and -0.144, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.405 and -0.180, respectively.

(4) Preparation of developer for electrostatic latent image

4 parts by weight of the yellow toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Example 22

(1) Coloring particle preparation

Similarly to Example 17 except for using different conditions of milling and classification, magenta coloring particles whose pigment average disperse size in the binder resin is $0.18\text{ }\mu\text{m}$ as a circle diameter and whose volume average particle size of the coloring particle is $3.2\text{ }\mu\text{m}$, and in which the particles having a size of $5.0\text{ }\mu\text{m}$ or more are present in the amount of 0.8% by number, the particles having a size of $4.0\text{ }\mu\text{m}$ or less in the amount of 90% by number, and the particles having a size of $1.0\text{ }\mu\text{m}$ or less in the amount of 4% by number are produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particles obtained above, 1.2 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particle: 15%) and 0.9 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 15%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20°C . and 50% humidity, the peak value is -0.297 and the bottom value is -0.045 . When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.198 and 0.018 , respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.405 and 0.072 , respectively.

(3) Preparation of developer for electrostatic latent image

4 parts by weight of the magenta toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Example 23

(1) Coloring particle preparation

Similarly to Example 17 except for using different conditions of milling and classification, magenta coloring particles whose pigment average disperse size in the binder resin is $0.18\text{ }\mu\text{m}$ as a circle diameter and whose volume average particle size of the coloring particle is $3.2\text{ }\mu\text{m}$, and in which the particles having a size of $5.0\text{ }\mu\text{m}$ or more are present in the amount of 1% by number, the particles having a size of $4.0\text{ }\mu\text{m}$ or less in the amount of 90% by number, and the particles having a size of $1.0\text{ }\mu\text{m}$ or less in the amount of 6% by number are produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particles obtained above and 2.5 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value

at 20°C . and 50% humidity, the peak value is -0.423 and the bottom value is 0.108 . When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.360 and 0.090 , respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.495 and 0.126 , respectively.

(3) Preparation of developer for electrostatic latent image

4 parts by weight of the magenta toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Comparative Example 13

(1) Coloring particle preparation

Similarly to Example 16 except for using different conditions of milling and classification, black coloring particles whose volume average particle size of the coloring particles is $8.2\text{ }\mu\text{m}$, in which the particles having a size of $5.0\text{ }\mu\text{m}$ or more are present in the amount of 90.1% by number, the particles having a size of $4.0\text{ }\mu\text{m}$ or less in the amount of 4.2% by number, and the particles having a size of $1.0\text{ }\mu\text{m}$ or less in the amount of 0% by number is produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the black coloring particles obtained above, 0.8 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 25%) and 0.7 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a black toner.

When the black toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20°C . and 50% humidity, the peak value is -0.585 and the bottom value is -0.369 . When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.549 and -0.342 , respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.648 and -0.395 , respectively.

(3) Preparation of developer for electrostatic latent image

8 parts by weight of the black toner obtained is mixed with 92 parts by weight of the carrier prepared in Carrier preparation 1 to produce a black two-component developer.

Using this two-component developer, the various evaluations summarized below are made.

Comparative Example 14

(1) Coloring particle preparation

Similarly to Example 16 except for using different conditions of milling and classification, black coloring particles whose volume average particle size of the coloring particle is $5.1\text{ }\mu\text{m}$, in which the particles having a size of $5.0\text{ }\mu\text{m}$ or more are present in the amount of 23.1% by number, the particles having a size of $4.0\text{ }\mu\text{m}$ or less in the amount of

54% by number, and the particles having a size of 1.0 μm or less in the amount of 0% by number is produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the black coloring particles obtained above, 1.8 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 35%) and 1.1 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a black toner.

When the black toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.450 and the bottom value is -0.198. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.423 and -0.180, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.486 and -0.225, respectively.

(3) Preparation of developer for electrostatic latent image

5 parts by weight of the black toner obtained is mixed with 95 parts by weight of the carrier prepared in Carrier preparation 1 to produce a black two-component developer.

Using this two-component developer, the various evaluations summarized below are made.

Comparative Example 15

(1) Coloring particle preparation

Similarly to Example 17 except for using different conditions of milling and classification, magenta coloring particles whose pigment average disperse size in the binder resin is 0.3 μm or less as a circle diameter and whose volume average particle size of the coloring particle is 7.5 μm , and in which the particles having a size of 5.0 μm or more are present in the amount of 84.6% by number, the particles having a size of 4.0 μm or less in the amount of 5% by number, and the particles having a size of 1.0 μm or less in the amount of 0% by number are produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particles obtained above, 1.1 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 30%) and 0.8 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.558 and the bottom value is -0.369. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.549 and -0.360, respectively, and the peak value and the bottom value at the

low temperature and the low humidity are -0.585 and -0.378, respectively.

(3) Preparation of developer for electrostatic latent image

8 parts by weight of the magenta toner obtained is mixed with 92 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

Comparative Example 16

(1) Coloring particle preparation

Similarly to Example 20 except for using different conditions of milling and classification, cyan coloring particles whose pigment average disperse size in the binder resin is 0.3 μm or less as a circle diameter and whose volume average particle size of the coloring particles is 7.3 μm , and in which the particles having a size of 5.0 μm or more are present in the amount of 80.5% by number, the particles having a size of 4.0 μm or less in the amount of 9% by number, and the particles having a size of 1.0 μm or less in the amount of 0% by number are produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the cyan coloring particles obtained above, 1.1 parts by weight of silica (SiO_2) microparticles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 30%) and 0.8 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a cyan toner.

When the cyan toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.540 and the bottom value is -0.268. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.513 and -0.270, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.567 and -0.306, respectively.

(3) Preparation of developer for electrostatic latent image

8 parts by weight of the cyan toner obtained is mixed with 92 parts by weight of the carrier prepared in Carrier preparation 1 to produce a cyan developer.

Using this two-component developer, the various evaluations summarized below are made.

Comparative Example 17

(1) Coloring particle preparation

Similarly to Example 21 except for using different conditions of milling and classification, yellow coloring particles whose pigment average disperse size in the binder resin is 0.2 μm as a circle diameter and whose volume average particle size of the coloring particle is 7.7 μm , and in which the particles having a size of 5.0 μm or more are present in the amount of 86.2% by number, the particles having a size of 4.0 μm or less in the amount of 5% by number, and the particles having a size of 1.0 μm or less in the amount of 0% by number are produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the yellow coloring particles obtained above, 1.1 parts by weight of silica (SiO₂) micro-particles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particle: 30%) and 0.7 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 30%) are mixed in a Henschel mixer to prepare a yellow toner.

When the yellow toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.594 and the bottom value is -0.342. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.576 and -0.324, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.621 and -0.360, respectively.

(3) Preparation of developer for electrostatic latent image

8 parts by weight of the yellow toner obtained is mixed with 92 parts by weight of the carrier prepared in Carrier preparation 1 to produce a yellow developer.

Using this two-component developer, the various evaluations summarized below are made.

Comparative Example 18

(1) Coloring particle preparation

Similarly to Example 17 except for using different conditions of milling and classification, magenta coloring particles whose pigment average disperse size in the binder resin is 0.18 μm as a circle diameter and whose volume average particle size of the coloring particle is 3.2 μm, and in which the particles having a size of 5.0 μm or more are

present in the amount of 0.5% by number, the particles having a size of 4.0 μm or less in the amount of 95% by number, and the particles having a size of 1.0 μm or less in the amount of 25% by number are produced.

(2) Preparation of toner for developing electric latent image

100 parts by weight of the magenta coloring particles obtained above, 2.5 parts by weight of silica (SiO₂) micro-particles whose surface has been imparted with hydrophobicity using HMDS and whose primary particle size is 40 nm (true specific gravity: 2.2, coating rate based on the surface of the coloring particles: 30%) and 2.4 parts by weight of metatitanic acid compound microparticles obtained as in Example 16 (coating rate based on the surface of the coloring particles: 40%) are mixed in a Henschel mixer to prepare a magenta toner.

When the magenta toner thus obtained is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity, the peak value is -0.315 and the bottom value is 0.018. When the frequency distribution of the q/d value is determined similarly also at a high temperature and a high humidity and at a low temperature and a low humidity, the peak value and the bottom value at the high temperature and the high humidity are -0.297 and 0.000, respectively, and the peak value and the bottom value at the low temperature and the low humidity are -0.324 and 0.045, respectively.

(3) Preparation of developer for electrostatic latent image

4 Parts by weight of the magenta toner obtained is mixed with 96 parts by weight of the carrier prepared in Carrier preparation 1 to produce a magenta developer.

Using this two-component developer, the various evaluations summarized below are made.

The characteristics of the toners obtained in Examples 16 to 23 and Comparative Examples 13 to 18 are summarized in Table 4 and Table 5 shown below.

TABLE 4

Characteristics of Coloring Particle							
Example/ Comparative No.	particle size (μm)	Volume average	Particles larger	Particles of	Particles of	Colorant (Pigment particle)	
		than 5.0 μm (% by no.)	4.0 μm or less (% by no.)	1.0 μm or less (% by no.)	Color	Average disperse size	
Example	16	3.5	2.0	88	3	K	—
	17	3.0	0.7	92	5	M	0.18 μm
	18	3.0	0.7	92	5	M	0.18 μm
	19	3.0	0.6	92	5	M	0.18 μm
	20	3.2	0.9	90	6	C	0.1 μm
	21	3.5	2.2	88	8	Y	0.2 μm
	22	3.2	0.8	90	4	M	0.18 μm
	23	3.2	1.0	90	6	M	0.18 μm
Comp. Example	13	8.2	90.1	4.2	0	K	—
	14	5.1	23.1	54	0	K	—
	15	7.5	84.6	5	0	M	0.18 μm
	16	7.3	80.5	8	0	C	0.1 μm
	17	7.7	86.2	5	0	Y	0.2 μm
	18	3.2	0.5	95	25	M	0.18 μm

Legend for colors: K: Black, M: Magenta, C: Cyan, Y: Yellow

TABLE 5

										Frequency Distribution of Toner q/d			
Characteristics of Vehicle							20° C.		High Temp. and High RH Environment, 30° C. and 85%		Low Temp. and Low RH Environment, 10° C. and 15%		
Ultra				Super-Ultra			and 50% RH		RH		RH		
Microparticle			Microparticle				Peak	Btm.	Peak	Btm.	Peak	Btm.	
Ex./Comp. No.	①	②	③	①	②	③	Value	Value	Value	Value	Value	Value	
Ex.	16	A	40 nm	25%	B	20 nm	30%	-0.342	-0.513	-0.324	-0.144	-0.360	-0.171
	17	A	40 nm	35%	B	20 nm	40%	-0.351	-0.144	-0.324	-0.135	-0.376	-0.153
	18	A	40 nm	30%	B	20 nm	40%	-0.315	-0.153	-0.297	-0.144	-0.324	-0.162
	19	A	40 nm	45%	B	20 nm	30%	-0.414	-0.135	-0.378	-0.126	-0.459	-0.144
	20	A	40 nm	35%	B	20 nm	40%	-0.405	-0.144	-0.378	-0.135	-0.432	-0.162
	21	A	40 nm	35%	B	20 nm	40%	-0.369	-0.162	-0.351	-0.144	-0.405	-0.180
	22	A	40 nm	15%	B	20 nm	15%	-0.297	0.045	-0.198	0.018	-0.405	0.072
Comp. Ex.	23	A	40 nm	30%	—	—	—	-0.423	0.108	-0.360	0.090	-0.495	0.126
	13	A	40 nm	25%	B	20 nm	30%	-0.585	-0.369	-0.549	-0.342	-0.648	-0.396
	14	A	40 nm	35%	B	20 nm	30%	-0.450	-0.198	-0.423	-0.180	-0.486	-0.225
	15	A	40 nm	30%	B	20 nm	30%	-0.558	-0.369	-0.549	-0.360	-0.585	-0.378
	16	A	40 nm	30%	B	20 nm	30%	-0.540	-0.288	-0.513	-0.270	-0.567	-0.306
	17	A	40 nm	30%	B	20 nm	30%	-0.594	0.342	-0.576	-0.324	-0.621	-0.360
18	A	40 nm	30%	B	20 nm	40%	-0.315	0.018	-0.297	0.000	-0.324	0.045	

① Type

② Primary Particle Size

③ Coating Rate

A: HMDS-treated silica microparticle

B: Metatitanic acid compound is a reaction product of metatitanic acid with i-butyltrimethoxysilane

Methods for various evaluations in Experiment 2

Each two-component developer obtained in each of Examples 16 to 23 and Comparative Examples 13 to 18 is used to evaluate the characteristics of the toner as shown below.

In the following evaluations, an ordinary non-coat full color paper is employed as a transfer material, together with a modified model of A color 935 manufactured by FUJI XEROX (modified to control the voltage upon development by means of external power source, hereinafter simply referred to as modified A color 935) as an image forming device.

Powder flowability evaluation

At a high temperature and a high humidity (30° C. and 85% RH) and at a low temperature and a low humidity (10° C. and 15% RH), 2 g of a toner is placed on a sieve of 75 μ m mesh size, and subjected to 1 mm oscillation for 90 seconds to observe the behavior of falling powder, based on which the evaluation is made. The criteria for evaluation is as follows.

o: No toner remains on the sieve.

 Δ : A slight amount of the toner remains on the sieve.

x: A substantial amount of the toner remains on the sieve.

Gradation reproducibility evaluation

A gradation image whose % image area is 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or 100% is made and examined for its image density using X-Rite model 404 (manufactured by X-Rite Co., Ltd.) to evaluate the gradation. The images having 5% and 10% image area are observed also using VH-6200 microscope (*KEYENCE* Co., Ltd) at the magnification of 175 to evaluate the image reproducibility in a low % image area. Based on the results obtained in these tests, the gradation reproducibility is judged with the criteria for evaluation as shown below.

o: Both of the gradation and the image reproducibility in a low % image area are satisfactory.

Δ : The gradation reproducible range is somewhat limited and the image reproducibility in a low % image area is somewhat unstable.

x: The gradation reproducible range is limited and the image reproducibility in a low % image area is unstable.

Initial fogging evaluation

An image sample obtained at an initial stage of image forming is examined for fogging in a non-image area by evaluating the sample visually at a distance of 30 cm from the sample. Evaluation is made with the criteria shown below.

o: No fogging.

 Δ : A slight fogging.

x: A substantial fogging.

Minute line reproducibility evaluation

Line interruption and edge sharpness when a 60 μ m minute line image is formed are observed using a digital microscope model VH-6220 (*KEYENCE* Co., Ltd), Evaluation is made with the criteria as shown below.

o: Minute lines are filled uniformly with the toner and no disturbed edges are observed.

Δ : Minute lines are filled almost uniformly with the toner but slightly jagged edges are observed.

x: Minute lines are not filled with the toner. Jagged edges are observed very evidently.

Image uniformity evaluation

The degree of the irregularity of the surface due to the difference in height between an imaged area and a non-imaged area is evaluated visually. The evaluation is made with the criteria shown below.

o: Uniformity is equivalent to that of offset printing.

 Δ : Uniformity is slightly lower than that of offset printing.

x: Uniformity is markedly lower than that of offset printing.

Cleanability

Cleanability is designated as ○ when no poor cleaning occurs during reproducing 3,000 copies, and as × when it occurs.

Overall evaluation

Based on the results of various evaluations as described above, the toners are subjected to overall evaluation. The evaluation is made with the criteria shown below.

○: Satisfactory for all evaluation items.

×: The results are designated as "Δ" for at least one evaluation item.

The results of the evaluation of the toners obtained in Examples 16 to 23 and Comparative Examples 13 to 18 are summarized in Table 6 shown below.

TABLE 6

Ex./Comp. No.	Powder Flowability		Initial Fogging	Gradation Reproducibility	Minute Line Reproducibility	Image Uniformity	Cleanability	Overall Evaluation
	High Temp. & High Humidity	Low Temp. & Low Humidity						
Ex. 16	○	○	○	○	⊙	○	○	○
17	○	○	○	○	⊙	○	○	○
18	○	○	○	○	⊙	○	○	○
19	○	○	○	○	⊙	○	○	○
20	○	○	○	○	⊙	○	○	○
21	○	○	○	○	⊙	○	○	○
22	×	Δ	Δ	○	⊙	Δ	○	×
23	Δ	Δ	Δ	○	⊙	Δ	○	×
Comp. Ex. 13	○	○	○	×	×	×	○	×
14	○	○	○	Δ	Δ	Δ	○	×
15	○	○	○	×	×	×	○	×
16	○	○	○	×	×	×	○	×
17	○	○	○	×	×	×	○	×
18	Δ	Δ	Δ	○	⊙	Δ	×	×

Example 24

Each of black, magenta, cyan and yellow developers prepared in Examples 16, 17, 20 and 21, respectively, is subjected to copy test. The copy test is performed using modified A color 935 as an image forming device.

The developers are subjected to evaluation for full color image characteristics (minute line reproducibility, image uniformity) and also to overall evaluation. The methods and the criteria for evaluation are similar to those for Examples 16 to 23 and Comparative Examples 13 to 18. The results are indicated in Table 7 shown below.

Comparative Example 19

Each of black, magenta, cyan and yellow developers prepared in Comparative Examples 13, 15, 16 and 17, respectively, is subjected to the copy test and the evaluation similar to those in Example 24. The results are indicated in Table 7 shown below.

TABLE 7

Ex./Comp. No.	Full Color Image Characteristics		Overall Evaluation
	Minute Line Reproducibility	Image Uniformity	
Example 24	⊙	○	○
Comparative Ex. 19	×	×	×

Discussion on results of Experiment 2

Based on the results described above, a toner for developing an electrostatic latent image according to the present

invention exhibits a high environmental stability and a satisfactory powder flowability, and serves to form an image exhibiting excellence in minute line reproducibility, gradation reproducibility and image uniformity without fogging.

Thus the toner of any of Examples 16 to 23 of the present invention allows an extremely satisfactory image quality to be obtained constantly, and in Example 24 utilizing such toners to form a full color image, a satisfactory full color image exhibiting excellent minute line reproducibility without unusual impression due to the image thickness is obtained even when three colors are overlaid.

It should be noted here that Examples 22 and 23 correspond to toners in accordance with the first aspect of the present invention, although these toners do not satisfy the

more preferred values of q/d in its frequency distribution. The toners of Examples 22 and 23 still exhibit excellent minute line reproducibility and gradation reproducibility, although fogging is observed.

To the contrary, the coloring particles having a large volume average particle size of each of Comparative Examples 13 to 17 fail to provide a satisfactory image quality due to reduction in minute line reproducibility, gradation reproducibility and image uniformity, although it has almost no problems with regard to environmental stability, powder flowability or fogging. Also in Comparative Example 18, minute line reproducibility and gradation reproducibility are satisfactory but fogging is observed. This may be because of the positive bottom value of the q/d in its frequency distribution. Comparative Example 19, in which a toner having no aspect of the present invention as described above is used to form a full color image, underwent further reduction in minute line reproducibility due to overlaying three colors, accompanied with unusual impression due to the image thickness, thus failing to provide a satisfactory full color image.

Experiment 3**Examples 25 to 35 and Comparative Examples 20 to 25****(1) Preparation of flushing pigment****Magenta flushing pigment**

70 parts by weight of polyester resin A (bisphenol-A polyester, weight average molecular weight: 11,000, number average molecular weight: 3,500, Tg: 65° C.) and 75 parts by weight of a magenta pigment (C.I. Pigment Red 57: 1)

hydrated paste (% pigment, 62% by weight) are placed in a kneader and mixed with heating gently. Kneading is continued at 120° C., and, after allowing to separate the aqueous layer from the resin layer, water is removed and the resin layer is further kneaded to remove water, and dehydrated to obtain a magenta flushing pigment.

Cyan flushing pigment

A cyan flushing pigment is obtained in the manner similar to that employed for the magenta flushing pigment except for using a cyan pigment (C.I. Pigment Blue 15:3) hydrated paste (% pigment, 62% by weight) instead of the magenta pigment hydrated paste.

Yellow flushing pigment

A yellow flushing pigment is obtained in the manner similar to that employed for the magenta flushing pigment except for using a yellow pigment (C.I. Pigment Yellow 17) hydrated paste (% pigment, 62% by weight) instead of the magenta pigment hydrated paste.

(2) Preparation of coloring particle

Coloring particle preparation 1

Polyester resin (bisphenol-A polyester, weight average molecular weight: 11,000, number average molecular weight: 3,500, Tg: 65° C.) 75 parts by weight

Magenta pigment described above 25 parts by weight

The components shown above are kneaded by a Banbury mixer, cooled, milled by a jet mill and then classified by a blower to produce the coloring particles in different conditions of milling and classification, namely, coloring particle A, B, F and L which have respective particle size distributions shown in Table 8.

Coloring particle preparation 2

Coloring particle D indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 1 except for using the cyan flushing pigment instead of the magenta flushing pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 3

Coloring particle E indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 1 except for using 70 parts by weight of the polyester resin and using 30 parts by weight of the yellow flushing pigment instead of 25 parts by weight of the magenta flushing

pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 4

Coloring particle C indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 1 except for using 91 parts by weight of the polyester resin and using 9 parts by weight of a carbon black (average primary particle size: 40 nm) instead of 25 parts by weight of the magenta flushing pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 5

Coloring particle G indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 1 except for using 80 parts by weight of the polyester resin and 20 parts by weight of the magenta flushing pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 6

Coloring particle H indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 1 except for using 90 parts by weight of the polyester resin and 10 parts by weight of the magenta flushing pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 7

Coloring particle J indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 2 except for using 90 parts by weight of the polyester resin and 10 parts by weight of the cyan flushing pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 8

Coloring particle K indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 3 except for using 88.5 parts by weight of the polyester resin and 12.5 parts by weight of the yellow flushing pigment. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

Coloring particle preparation 9

Coloring particle I indicated in Table 8 is obtained in the manner similar to that in Coloring particle preparation 4 except for using 97 parts by weight of the polyester resin and 3 parts by weight of the carbon black. The conditions of milling and classification are adjusted to obtain the particle size distribution shown in Table 8.

TABLE 8

Type of Coloring Particle	Volume Average Particle Size (μm)	Particles Larger Than 5.0 μm (% by number)	Particles of 4.0 μm or less (% by number)	Particles of 1.0 μm or less (% by number)	Color or Colorant
Coloring Particle A	3.2	0.8	96.4	3.8	M
Coloring Particle B	3.6	2.2	89.6	3.0	M
Coloring Particle C	3.5	1.8	91.5	3.2	K
Coloring Particle D	3.6	1.6	90.8	2.9	C
Coloring Particle E	3.6	1.7	90.6	2.9	Y
Coloring Particle F	4.4	8.9	76.2	2.1	M
Coloring Particle G	5.7	28.4	44.3	1.8	M
Coloring Particle H	7.8	84.1	8.2	0.4	M
Coloring Particle I	8.2	89.2	4.7	0.3	K
Coloring Particle J	7.5	80.1	9.6	0.4	C
Coloring Particle K	7.6	81.1	9.1	0.5	Y
Coloring Particle L	2.8	1.0	99.1	25.4	M

Legend for colors: K: Black, M: Magenta, C: Cyan, Y: Yellow

Preparation of toner for developing electrostatic latent image
(1) Additives

In Experiment 3, ultra microparticles A and super-ultra microparticles B to E shown below are employed as external additive components.

A: Silica microparticles whose surface is imparted with hydrophobicity using HMDS (SiO_2 , primary average particle size: 40 nm, true specific gravity: 2.2)

B: Silica microparticles whose surface is imparted with hydrophobicity using HMDS (SiO_2 , primary average particle size: 20 nm, true specific gravity: 2.2)

C: Metatitanic acid microparticles whose surface is imparted with hydrophobicity using i-butyltrimethoxysilane (primary average particle size: 25 nm, true specific gravity: 3.2)

D: Metatitanic acid microparticles whose surface is imparted with hydrophobicity using i-butyltrimethoxysilane and fluorosilane (primary average particle size: 25 nm, true specific gravity: 3.2)

E: Rutile type titanium oxide microparticle whose surface is imparted with hydrophobicity using decylsilane (primary average particle size: 25 nm, true specific gravity: 3.9)

(2) Toner preparation

Coloring particles A to G are mixed in a Henschel mixer with Additive components A to E in the combinations and in the condition indicated in Table 9 shown below to produce Toners 1 to 17.

Each of Toners 1 to 17 is examined by the CSG method for the frequency distribution of the q/d value at 20° C. and 50% humidity. Each of Toners 1 to 17 are also examined for the aggregation degree. The results are summarized in Table 9 shown below.

TABLE 9

Toner	Coloring Particle	Vehicle Components						Frequency Distribution of toner q/d		
		Ultra			Super-Ultra			(20° C. and 50% RH)		
		Microparticles			Microparticles			Peak	Bottom	Aggregation
		①	②	③	①	②	③	Value	Value	Degree
Toner 1	Coloring Particle A	A	40 nm	40%	D	25 nm	40%	-0.315	-0.144	15.4
Toner 2	Coloring Particle B	A	40 nm	40%	D	25 nm	40%	-0.360	-0.180	12.8
Toner 3	Coloring Particle C	A	40 nm	40%	D	25 nm	40%	-0.351	-0.171	11.9
Toner 4	Coloring Particle D	A	40 nm	40%	D	25 nm	40%	-0.342	-0.162	12.2
Toner 5	Coloring Particle E	A	40 nm	40%	C	25 nm	40%	-0.450	-0.216	12.9
Toner 6	Coloring Particle F	A	40 nm	40%	D	25 nm	40%	-0.450	-0.243	10.7
Toner 7	Coloring Particle B	A	40 nm	15%	D	25 nm	30%	-0.342	-0.216	10.6
Toner 8	Coloring Particle B	A	40 nm	40%	E	25 nm	40%	-0.261	-0.108	28.9
Toner 9	Coloring Particle G	A	40 nm	20%	C	25 nm	35%	-0.486	-0.270	10.2
Toner 10	Coloring Particle H	A	40 nm	20%	E	25 nm	35%	-0.558	-0.315	8.1
Toner 11	Coloring Particle I	A	40 nm	20%	D	25 nm	35%	-0.648	-0.360	7.2
Toner 12	Coloring Particle J	A	40 nm	20%	D	25 nm	35%	-0.576	-0.297	8.5
Toner 13	Coloring Particle K	A	40 nm	20%	D	25 nm	35%	-0.684	-0.432	8.3
Toner 14	Coloring Particle B	A	40 nm	40%	—	—	—	-0.342	0.072	42.1
Toner 15	Coloring Particle L	A	40 nm	40%	D	25 nm	40%	-0.288	0.000	25.4
Toner 16	Coloring Particle F	—	—	—	B	20 nm	100%	-1.008	-0.045	6.9
Toner 17	Coloring Particle B	A	40 nm	10%	C	25 nm	10%	-0.189	0.036	31.2

① Type

② Primary Particle Size

③ Coating Rate

60

Carrier preparation

Carrier a

Carrier a is obtained in the manner similar to that in Carrier preparation 1 except for using Cu—Zn ferrite microparticle having the volume average particle size of 35 μm instead of Cu—Zn ferrite microparticle having the volume

average particle size of 40 μm employed in Carrier preparation 1 in Experiment 1 described above.

Carrier b

Carrier b is obtained in the manner similar to that in Carrier preparation 1 except for using γ -aminopropyltriethoxysilane in the amount of 0.5 parts by weight instead of 0.1 parts by weight employed in Carrier preparation 1 in Experiment 1 described above.

Example 25

A two-component developer (2-1) is produced by mixing 100 parts by weight of Carrier a and 4 parts by weight of Toner 1 using a V-mixer.

Example 26

A two-component developer (2-2) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 2 instead of 4 parts by weight of Toner 1.

Example 27

A two-component developer (2-3) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 3 instead of 4 parts by weight of Toner 1.

Example 28

A two-component developer (2-4) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 4 instead of 4 parts by weight of Toner 1.

Example 29

A two-component developer (2-5) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 5 instead of 4 parts by weight of Toner 1.

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Example 30

A two-component developer (2-6) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 6 instead of 4 parts by weight of Toner 1.

Example 31

A two-component developer (2-7) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 7 instead of 4 parts by weight of Toner 1.

Example 32

A two-component developer (2-8) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 8 instead of 4 parts by weight of Toner 1.

Example 33

A two-component developer (2-14) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 14 instead of 8 parts by weight of Toner 1.

Example 34

A two-component developer (2-16) is produced in the manner similar to that in Example 25 except for using Carrier b instead of Carrier a and using 5 parts by weight of Toner 16 instead of 8 parts by weight of Toner 1.

Example 35

A two-component developer (2-17) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 17 instead of 8 parts by weight of Toner 1.

Comparative Example 20

A two-component developer (2-9) is produced in the manner similar to that in Example 25 except for using 6 parts by weight of Toner 9 instead of 4 parts by weight of Toner 1.

Comparative Example 21

A two-component developer (2-10) is produced in the manner similar to that in Example 25 except for using 8 parts by weight of Toner 10 instead of 4 parts by weight of Toner 1.

Comparative Example 22

A two-component developer (2-11) is produced in the manner similar to that in Example 25 except for using 8 parts by weight of Toner 11 instead of 4 parts by weight of Toner 1.

Comparative Example 23

A two-component developer (2-12) is produced in the manner similar to that in Example 25 except for using 8 parts by weight of Toner 12 instead of 8 parts by weight of Toner 1.

Comparative Example 24

A two-component developer (2-13) is produced in the manner similar to that in Example 25 except for using 8 parts by weight of Toner 13 instead of 8 parts by weight of Toner 1.

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Comparative Example 25

A two-component developer (2-15) is produced in the manner similar to that in Example 25 except for using 4 parts by weight of Toner 15 instead of 8 parts by weight of Toner 1.

Methods for various evaluations in Experiment 3

Each of two-component developers (2-1) to (2-17) obtained in Examples 25 to 35 and Comparative Examples 20 to 25 is evaluated using modified A-color 935 at 22° C/55% RH. J Coat paper (FUJI XEROX) is used and the condition of the device is adjusted so that the image density of an image having the image area of 100% is 1.5 or more after fixing.

Initial fogging evaluation

An image sample obtained at an initial stage of image forming is examined for fogging in a non-image area by evaluating the sample visually at a distance of 30 cm from the sample. Evaluation is made with the criteria shown below. The results indicated by ⊙ and ○ are considered to be acceptable.

⊙: No fogging.

○: A slight fogging is noted when observed closely.

Δ: A fogging is somewhat evident.

×: A fogging is evident.

××: A fogging is very evident.

Minute line reproducibility evaluation

A line image is formed at the line interval of 50 μm on a photoconductor, and transferred to a transfer material and then fixed. The line image formed on the transfer material is observed using model VH-6220 Microhighscope (*KEYENCE* Co., Ltd) at the magnification of 175. Evaluation is made with the criteria as shown below. The results indicated by G1 and G2 are considered to be acceptable.

G1: Minute lines are filled uniformly with the toner and no disturbed edges are observed.

G2: Minute lines are filled uniformly with the toner but slightly jagged edges are observed.

G3: Minute lines are filled uniformly with the toner but jagged edges are observed evidently.

G4: Minute lines are not filled uniformly with the toner and jagged edges are observed evidently.

G5: Minute lines are not filled uniformly with the toner and jagged edges are observed very evidently.

Transfer efficiency evaluation

A 2 cm×5 cm solid patch is developed and transferred, and then the toner remaining on the photoconductor is transferred onto a tape and weighed to obtain the residual toner amount, α(g), and the transferred toner amount, β(g), is also obtained by weighing the toner on the paper, and then the transfer efficiency (%) is calculated according to the equation shown below.

$$\text{Transfer efficiency (\%)} = \beta / (\alpha + \beta) \times 100$$

Solid image uniformity evaluation

An image is evaluated visually and judged as any one of degrees G1 (Good) to G5 (Poor) with reference to a limit sample. The results indicated by G1 and G2 are considered to be acceptable.

Gradation reproducibility evaluation

A gradation image whose % image area is 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% or 100% is made and examined for its image density using X-Rite model 404 (manufactured by X-Rite Co., Ltd.) to evaluate the

gradation. The images having 5% and 10% image area are observed also using VH-6200 microscope (*KEYENCE* Co., Ltd) at the magnification of 175 to evaluate the image reproducibility in a low % image area. Based on the results obtained in these tests, the gradation reproducibility is judged with the criteria for evaluation as shown below.

G1: Both of the gradation and the image reproducibility in a low % image area are satisfactory.

G2: Satisfactory gradation is obtained but the image in a low % image area are somewhat unstable.

G3: The gradation reproducible range is somewhat limited in a low % image area and the image in a low % image area is somewhat unstable.

G4: The gradation reproducible range is somewhat limited in high and low % image areas and the image in a low % image area is somewhat unstable.

G5: The gradation reproducible range is limited in high and low % image areas and the image in a low % image area is unstable.

Cleanability

Cleanability is designated as ○ when no poor cleaning occurs during reproducing 3,000 copies, and as × when it occurs.

The results of the evaluations described above are summarized in Table 10 and Table 11 shown below.

TABLE 10

Developer for Electrostatic Latent Image						Results		
		Toner		Carrier		Initial	Minute Line	Transfer
Ex./Comp. No.	No.	Parts by Weight	Type	Parts by Weight		Fogging	Reproducibility	Efficiency (%)
Ex.	25	1	4	a	100	⊙	G1	91.8
	26	2	4	a	100	⊙	G1	92.5
	27	3	4	a	100	⊙	G1	93.0
	28	4	4	a	100	⊙	G1	92.7
	29	5	4	a	100	⊙	G1	91.8
	30	6	5	a	100	⊙	G2	93.6
	31	7	4	a	100	⊙	G1	85.6
	32	8	4	a	100	○	G1	90.7
	33	14	4	a	100	XXX	G1	88.7
	34	16	5	b	100	○	G3	71.2
	35	17	4	a	100	X	G1	79.4
	20	9	6	a	100	⊙	G3	91.2
	21	10	8	a	100	⊙	G4	93.2
	22	11	8	a	100	⊙	G4.5	94.4
	23	12	8	a	100	○	G4	92.6
Comp. Ex.	24	13	8	a	100	⊙	G4	91.8
	25	15	4	a	100	Δ	G1	88.9

TABLE 11

Developer for Electrostatic Latent Image						Results		
		Toner		Carrier		Solid Image	Gradation	
Ex./Comp. No.	No.	Parts by Weight	Type	Parts by Weight		Uniformity	Reproducibility	Cleanability
Ex.	25	1	4	a	100	G1	G1	○
	26	2	4	a	100	G1	G1	○
	27	3	4	a	100	G1	G1	○
	28	4	4	a	100	G1	G1	○
	29	5	4	a	100	G1	G1	○
	30	6	5	a	100	G2	G2	○
	31	7	4	a	100	G1	G1	○
	32	8	4	a	100	G1	G1	○
	33	14	4	a	100	G2	G2	○
	34	16	5	b	100	G4	G3	○
	35	17	4	a	100	G1	G2	○
	20	9	6	a	100	G3	G3	○
	21	10	8	a	100	G4	G5	○
	22	11	8	a	100	G4	G5	○
	23	12	8	a	100	G4	G5	○
Comp. Ex.	24	13	8	a	100	G4	G5	○
	25	15	4	a	100	G1	G1	X

Based on the results described above, a toner for developing an electric latent image according to the present invention can provide an image which is free from initial fogging, exhibits excellent minute line reproducibility and gradation reproducibility, achieves a higher efficiency and provides a uniform solid image.

Accordingly, by using a toner obtained in any of Examples 25 to 30 and 32, a very satisfactory image quality can be achieved. The toner obtained in Example 30 exhibits the minute line reproducibility which is somewhat lower than those in other examples, because of a slightly larger volume average particle size of the coloring particles. The toner obtained in Example 32 exhibits poorer results with regard to the initial fogging when compared with other Examples, because of the bottom value of the q/d frequency distribution which is slightly more near zero value than in other Examples, as well as a slightly higher aggregation degree of the toner. Nevertheless, both Examples 30 and 32 are well within the acceptable range.

Also when using the toner obtained in Example 31, an image of a satisfactory quality is obtained, but the transfer efficiency is slightly poorer when compared with other Examples due to a smaller amount of the ultra microparticle being added as an external additive than in other Examples. Nevertheless, the toner is well within the acceptable range.

As to Examples 33-35, these Examples have the preferred particle size and particle size distribution for the coloring particles according to the first aspect, but do not have the more preferred aspect with respect to the external additive. Example 33 contains no super-ultra microparticles while Example 34 contains no ultra microparticles. Example 35 does not satisfy the external additive coating rates. Example 34 also lacks the more preferred q/d frequency distribution since it has a larger absolute value of the peak value of the q/d frequency distribution. However, these Examples still exhibit excellent minute line reproducibility and cleanliness, although the transfer efficiency is lower.

To the contrary, any of the coloring particles in Comparative Examples 20 to 24 which have larger particle sizes result in an image which is not satisfactory due to its poor minute line reproducibility and poor solid image uniformity, although it has no problems with regard to the initial fogging or the transfer efficiency.

Comparative Example 25 exhibits improved minute line reproducibility and solid image uniformity due to a sufficiently reduced volume average particle sizes, it is not satisfactory with regard to the initial fogging and/or the transfer efficiency since it lacks the preferred q/d frequency distribution and external additive properties. In this Comparative Example, as well as Examples 33 and 35 above, the bottom values of the frequency distributions of the q/d values are positive values. Comparative Example 28 in which coloring particles of a size exceeding $1.0 \mu\text{m}$ are present in an amount exceeding 20% by number also does not have the preferred particle size distribution. Accordingly, it exhibits initial fogging.

A toner for developing an electric latent image according to the present invention exhibits excellent minute line reproducibility and gradation, provides an image without fogging, and has an excellent durability. Also according to the present invention, a toner for developing an electrostatic latent image whose charging characteristics are not subjected to the effects of temperature and humidity, which is readily charged and which maintains a sharp charge distribution even when a toner is newly added into the developing unit can be provided, and thus is suitable especially in the development of a digital latent image.

By employing a toner for developing an electrostatic latent image and a method for forming an image using the same according to the present invention, an image quality as high as that by achieved offset printing or even higher can be achieved.

Experiment 4

Examples 36-40 and Comparative Examples 26-28

Carrier Preparation

100 parts by weight of a Cu-Zn ferrite microparticle having a volume average particle size of $40 \mu\text{m}$ is admixed with a methanol solution of 0.1 parts by weight of (α -aminopropyltriethoxysilane and coating is effected using a kneader, methanol is distilled off, and then the above silane compound is hardened completely by heating for 2 hours at 120°C . The particles are admixed with perfluorooctylethyl methacrylate-methyl methacrylate copolymer (copolymerization ratio, 40:60 by weight) dissolved in toluene and subjected to a vacuum kneader to yield a resin-coated carrier having 0.5% by weight of the perfluorooctylethyl methacrylate-methyl methacrylate copolymer as a coating thereon.

Non-color transparent toner preparation

Polyester resin A is pulverized and classified to yield non-color transparent particles having a volume average size of $5 \mu\text{m}$. 100 parts by weight of the non-color transparent particles obtained are mixed with 0.98 parts by weight of a silica (SiO_2) microparticle whose surface has been imparted with hydrophobicity using hexamethyldisilazane and whose average primary particle size is 40 nm (true specific gravity: 2.2) and 1.26 parts by weight of metatitanic acid compound microparticle which is the reaction product between metatitanic acid and *i*-butyltrimethoxysilane (20 parts by weight *i*-butyltrimethoxysilane to 10 parts by weight of metatitanic acid) and whose average primary particle size is 20 nm (true specific gravity: 3.2) in a Henschel mixer to yield a non-color transparent toner.

The Polyester A described above is a bisphenol-A ethylene oxide adduct/cyclohexane dimethanol/terephthalic acid having a molecular weight $M_w=1,000$, $M_n=3,500$, glass transition point= 65°C . and softening point= 105°C .

Metatitanic acid and *i*-butyltrimethoxysilane are reacted as described below. Thus, metatitanic acid slurry is admixed with 4 N aqueous solution of sodium hydroxide, adjusted to a pH 9.0, stirred and then neutralized with 6 N hydrochloric acid. The mixture is filtered and the materials obtained on the filter are washed with water and combined again with water to form a slurry, which is adjusted to a pH 1.2 with 6 N hydrochloric acid, and stirred for a certain period to effect peptization. The peptized slurry thus obtained is combined with *i*-butyltrimethoxysilane, stirred for a certain period, and then neutralized with 8 N aqueous solution of sodium hydroxide. The mixture is filtered and the materials obtained on the filter are washed with water, dried at 150°C ., milled using a jet mill, separated from coarse particles, thereby obtaining a metatitanic acid compound microparticle which is the reaction product between metatitanic acid and *i*-butyltrimethoxysilane and whose average primary particle size is 20 nm .

White Toner Preparation

Polyester resin A 80 parts by weight

Rutile type titanium oxide (average

primary particle size: $0.25 \mu\text{m}$) 20 parts by weight

The mixture comprising the above components is made molten and kneaded. The kneaded mixture is cooled, pul-

verized and classified to yield white particles having an volume average particle size of 5 μm . 100 parts by weight of the white particles are mixed with 0.98 parts by weight of a silica microparticles whose surface has been imparted with hydrophobicity using hexamethyldisilazane and whose average primary particle is 40 nm and 1.26 parts by weight of the above metatitanic acid compound microparticles in a Henschel mixer to yield a white toner.

Preparation of developer for surface-smoothing step

100 parts by weight of resin-coated type carrier prepared in the above described carrier preparation is mixed with each of 3 parts by weight of the both toners obtained in the above described non-color toner preparation and white toner preparation, respectively, to yield non-color transparent and white developers for use in the surface-smoothing step.

Preparation of developers for electrostatic latent image

A. Color toner Preparation

(1) Preparation of flushing pigment

Magenta flushing pigment

70 parts by weight of polyester resin (bisphenol-A type polyester: bisphenol A ethylene oxide adduct-cyclohexane dimethanol-terephthalic acid, molecular weight $M_w=1$ 1,000, $M_n=3,500$, glass transition point $=65^\circ\text{C}$. and 75 parts by weight of a magenta pigment (C.I. Pigment Red 57:1) hydrated paste (% pigment, 40% by weight) are placed in a kneader and mixed with heating gently. Kneading is continued at 120°C ., and, after allowing to separate the aqueous layer from the resin layer, water is removed and the resin phase is further kneaded to remove water, and dehydrated to obtain a magenta flushing pigment.

Cyan flushing pigment

Cyan flushing pigment is prepared in the same manner as the magenta flushing pigment except that cyan pigment (C.I. pigment blue 15:3) hydrated paste (% pigment, 40% by weight) is used in place of the magenta pigment hydrated paste.

Yellow flushing pigment

Yellow flushing pigment is prepared in the same manner as the magenta flushing pigment except that yellow pigment (C.I. pigment yellow 17) hydrated paste (% pigment, 40% by weight) is used in place of the magenta pigment hydrated paste.

(2) Preparation of coloring particle

Preparation 1 of coloring particle

Polyester resin (bisphenol-A type polyester: bisphenol A ethylene oxide adduct-cyclohexane dimethanol-terephthalic acid, molecular weight $M_w=1$ 1,000, $M_n=3,500$, glass transition point $=65^\circ\text{C}$.) 66.7 parts by weight

The above cyan flushing pigment (% pigment, 40% by weight)

33.3 parts by weight

The above components are made molten and kneaded with Banbury mixer, cooled, pulverized with a jet mill and classified with an air classifier to yield a coloring particle C1. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

The particle size and the particle size distribution are determined using a Coulter counter model TA-II manufactured by Coulter Co., Ltd. In this determination, a 100 μm aperture tube is used for a toner (coloring particle) having an average particle size exceeding 5 μm and a toner having an average particle size less than 5 μm is determined at the aperture size of 50 μm , and the frequency distribution of the particle having a size of 1 μm or less is determined at the aperture size of 30 μm . The particle size is determined similarly in the following Examples and Comparative Examples.

Preparation 2 of coloring particle

Coloring particle M1 shown in the following Table 12 is prepared in the same manner as described in the Preparation 1 of coloring particle except that magenta flushing pigment is used in place of cyan flushing pigment. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

Preparation 3 of coloring particle

Coloring particle Y1 shown in the following Table 12 is prepared in the same manner as described in the Preparation 1 of coloring particle except that 50 parts by weight of the polyester resin is used and that 50 parts by weight of yellow flushing pigment is used in place of 25 parts by weight of the cyan flushing pigment. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

Preparation 4 of coloring particle

Coloring particle K1 shown in the following Table 12 is prepared in the same manner as described in the Preparation 1 of coloring particle except that 90 parts by weight of the polyester resin is used and that 10 parts by weight of carbon black (primary particle average size: 40 nm) is used in place of 25 parts by weight of cyan flushing pigment. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

Preparation 5 of coloring particle

Coloring particle C2 shown in the following Table 12 is prepared in the same manner as described in the Preparation 1 of coloring particle except that 86.7 parts by weight of the polyester resin is used and that 13.3 parts by weight of the cyan flushing pigment is used. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

Preparation 6 of coloring particle

Coloring particle M2 shown in the following Table 12 is prepared in the same manner as described in the Preparation 2 of coloring particle except that 86.7 parts by weight of the polyester resin is used and that 13.3 parts by weight of the magenta flushing pigment is used. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

Preparation 7 of coloring particle

Coloring particle Y2 shown in the following Table 12 is prepared in the same manner as described in the Preparation 3 of coloring particle except that 83.3 parts by weight of the polyester resin is used and that 16.7 parts by weight of the yellow flushing pigment is used. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

Preparation 8 of coloring particle

Coloring particle K2 shown in the following Table 12 is prepared in the same manner as described in the Preparation 4 of coloring particle except that 97 parts by weight of the polyester resin is used and that 3 parts by weight of the carbon black is used. The conditions of pulverization and classification are controlled so as to have the particle size distribution shown in the following Table 12.

In the following Table 12, pigment concentration C (%) in each coloring particle, true specific gravity ρ of each coloring particle, ρ/ADC calculated from these values and the volume average particle size D (μm) of the coloring particles, and average particle size (circle diameter: μm) of dispersed particles in binder resin of pigment microparticles, as well as the description as regard to particle size of each coloring particle obtained above, are summarized.

TABLE 12

Coloring Particle	Volume Average Particle Size	Particle Exceeding 5.0 μm (% by number)	Particle of 1.0 to 2.5 μm (% by number)	Particle less than 1.0 μm (% by number)	Color of colorant*	Pigment concentration C (%)	True specific gravity a	aDC	Pigment dispersion size (μm)**
C1	3.6	1.6	38.0	2.9	C	10	1.24	44.5	0.23
M1	3.6	2.2	36.5	3.0	M	10	1.24	44.6	0.20
Y1	3.6	1.7	37.3	2.9	Y	15	1.25	67.5	0.20
K1	3.5	2.0	41.2	3.0	K	10	1.20	42.0	—
C2	7.5	78.0	0.0	0.0	C	4	1.22	36.0	0.21
M2	7.8	80.1	0.0	0.0	M	4	1.22	38.1	0.24
Y2	7.6	81.1	0.0	0.0	Y	5	1.21	46.0	0.24
K2	8.2	89.2	0.0	0.0	K	3	1.20	29.5	—

*color K: black, M: magenta, C: cyan, Y: yellow

**pigment dispersion size is an average particle size of dispersion particle in a binder resin of pigment microparticles (circle diameter: μm)

(3) Preparation of Color toner

Each of the above described coloring particles is admixed with a silica (SiO_2) microparticle whose surface has been imparted with hydrophobicity using hexamethyldisilazane (HMDS) and whose average primary particle size is 40 nm and metatitanic acid compound microparticle which is the reaction product between metatitanic acid and i-butyltrimethoxysilane and whose average primary particle size is 20 nm so as to have a coating rate to the surface of each of the coloring particles of 40%, and mixed in a Henschel mixer to yield color toners C1 and 2, M1 and 2, Y1 and 2, and K1 and 2, respectively. The symbols of C1 and 2, M1 and 2, Y1 and 2, and K1 and 2 attached to each color toner obtained correspond to each of the symbols of C1 and 2, M1 and 2, Y1 and 2, and K1 and 2 of the coloring particles used, respectively.

The term coating rate to the surface of coloring particle means herein a value F (%) calculated by the above-mentioned Formula (1).

With respect to each of the color toners obtained, the frequency distribution of the q/d value is determined in an atmosphere of at a temperature of 20° C. and a humidity of 50 %. The each peak value and bottom value obtained are shown in the following Table 13.

TABLE 13

Toner	Frequency Distribution of q/d Value (20° C./50% RH)	
	Peak Value	Bottom Value
C1	-0.342	-0.162
M1	-0.360	-0.180
Y1	-0.450	-0.216
K1	-0.351	-0.171
C2	-0.576	-0.297
M2	-0.558	-0.315
Y2	-0.684	-0.432
K2	-0.648	-0.360

B. Preparation of a developer for electrostatic latent image

100 parts by weight of the resin-coated carrier prepared in the above described Carrier Preparation is mixed with 4 parts by weight of each of the toners C1, M1, Y1 and K1 obtained in the above described Preparation of color toner to yield a developer for electrostatic latent image C1, M1, Y1 and K1, respectively. Further, 100 parts by weight of the resin-coated carrier prepared in the above described Carrier Preparation is mixed with 8 parts by weight of each of the toners C2, M2, Y2 and K2 obtained in the above described

Preparation of color toner to yield a developer for electrostatic latent image C2, M2, Y2 and K2, respectively. The symbols of C1 and 2, M1 and 2, Y1 and 2, and K1 and 2 attached to each developer for electrostatic latent image obtained correspond to each of the symbols of C1 and 2, M1 and 2, Y1 and 2, and K1 and 2 of the color toners used, respectively.

Example 36

Copy test is made by using each of the above developers for electrostatic latent image C1, M1, Y1 and K1 for cyan, magenta, yellow and black as a developer and a coat paper for full-color printing (ten point average surface roughness $R_z=9 \mu\text{m}$, whiteness degree: 80%) as a transfer material, respectively. The copy test is carried out using a Modified A color 935 (manufactured by Fuji Xerox Co., Ltd.) as an image forming machine (which is modified so as to control electric voltage at the time of developing with an external power source), controlling parameters for developing and transferring properly, and forming each image described below. The content and results of evaluation tests are described below.

(Image 1)

4 kinds of single-color images (containing minute line having a line width of 50 μm in an image) which are primary color (single color) images of each color toner of cyan, magenta, yellow and black, are formed by developing, transferring and fixing so that the TMA on a transfer material on a region having an image area rate of 100% has the values for each color shown in the following Table 14.

(Image 2)

4 kinds of solid images having an image area rate of 100% and a minute line having a line width of 50 μm comprising each secondary color (3 kinds) of red, blue and green and tertiary color of process black (1 kind) are formed under the same conditions of developing of the each color toner as described above (Image 1).

(Image 3)

Gradation images are formed as to each single color (3 kinds) of cyan, magenta and yellow; each secondary color (3 kinds) of red, blue and green; tertiary color (1 kind) of process black under the same conditions of the each color toner as described above (Image 1). The gradation images formed are to have standards of image area rates of 5%, 15%, 30%, 50%, 75%, 80% and 90%.

(Image 4)

Picture images in which different image area rates images are intermixed, are formed under the same conditions of the each color toner as described above (Image 1).

The method for determining TMA on an area having an image area rate of 100% of a transfer material is as follows. Method for determining TMA on an area having an image area rate of 100% on a transfer material

Forming each image of primary, secondary and tertiary color having an image area rate of 100%, the parameters for developing and transferring are controlled so as to have an image density after fixing of 1.8, and a sample in an un-fixed state is extracted. The obtained un-fixed sample is weighed (A; mg), an un-fixed toner on a transfer material is removed off with air-blow, a weight of only the transfer material is determined (B; mg), the TMA (mg/cm²) is calculated from the weight difference of before and after of the removal of the un-fixed toner (A-B: mg).

Example 37

A copy test is made as in the same manner as Example 36 except that a coat paper for full-color printing (whiteness degree: 85%) having a ten point average surface roughness of Rz=5 μ m as a transfer material is used, the TMA values on an area having an image area rate of 100% on a transfer material of each single toner are controlled to have the values as shown in the following Table 14, and the developing conditions for each color toner for (Image 2) to (Image 4) are controlled to correspond to them.

Example 38

A modified A color 935 manufactured by Fuji Xerox Co., Ltd. is used as an image forming machine for copy test in which a surface-smoothing developing device which can form a non-color transparent toner or white color toner on a paper surface is incorporated. In the surface-smoothing developing device, a developer for surface-smoothing step is incorporated.

The image forming device has a structure which can form previously a layer comprising a non-color transparent toner or a white toner on the entirety of one side of a transfer material on which an image is to be formed before forming a full-color image. As a concrete structure, a solid image of a non-color transparent toner or a white toner is formed on an entirety of the surface of a latent image support with a surface-smoothing developing machine, and it is transferred to a transfer material to form a layer of a non-color transparent toner or a white toner.

On the transfer material on which a non-color transparent toner layer or a white toner layer is formed in this way, a toner image comprising color toner is transferred to be fixed in the fixing step. The non-color transparent toner layer or a white toner layer is heated to be fixed with a fixing roll in the step fixing toner image with color toners to cover the concave parts of the surface of the transfer material having a ten point average surface roughness Rz exceeding 10 μ m, so that the embedding of the color toners in the concave parts can be prevented effectively. The ten point average surface roughness Rz of the surface of the transfer material on which a non-color transparent toner layer or a white toner layer is formed, can be obtained by forming only a non-color transparent toner layer or a white toner layer is formed and determining it as to the surface of the transfer material on which it is fixed.

A copy test is made as in the same manner as described in Example 36, except that a developer for the surface-smoothing step (non-color and transparent) described in the Preparation of developer for the surface-smoothing step is used as a developer for surface-smoothing step, each of the developers of the above described developers for electro-

static latent image of C1, M1, Y1 and K1 of cyan, magenta, yellow and black is used as a developer for image forming, a coat paper for full-color printing (ten point average surface roughness Rz=9 μ m, whiteness degree: 80%) is used as a transfer material, the TMA value of a region having an image area rate of 100% of each single toner of (Image 1) in Example 36 on the transfer material is controlled to be a value shown in the following Table 14, and the developing conditions for each color toner of (Image 2) to (Image 4) are matched to it. The toner weight of the non-color transparent toner is 0.3 mg/cm², and the ten point average surface roughness Rz after forming the layer is 6 μ m, and the whiteness degree is 80%.

Example 39

A copy test is made as in the same manner as described in Example 36, except that the same image forming device similar as Example 38 is used, a developer for surface-smoothing step (white) described in the Preparation of developer for surface-smoothing step is used as a developer for surface-smoothing step, each of the developers of the above described electrostatic latent image developer C1, M1, Y1 and K1 of cyan, magenta, yellow and black is used as a developer for image forming, a coat paper for monochrome printing (ten point average surface roughness Rz=16 μ m, whiteness degree: 75%) is used as a transfer material, the TMA value of a region having an image area rate of 100% of each single toner of (Image 1) of Example 36 on the transfer material is controlled to be a value shown in the following Table 14, and the developing conditions for each color toner of (Image 2) to (Image 4) are matched to it. The toner weight of the non-color transparent toner is 0.4 mg/cm², and the ten point average surface roughness Rz after forming the layer is 9 μ m, and the whiteness degree is 89%.

Example 40

A copy test is made as in the same manner as described in Example 36, except that a non-coat paper for monochrome printing having ten point average surface roughness Rz=16 μ m (whiteness degree: 75%) is used as a transfer material, the TMA value of a region having an image area rate of 100% of each single toner of (Image 1) of Example 36 on the transfer material is controlled to be a value shown in the following Table 14, and the developing conditions for each color toner of (Image 2) to (Image 4) are matched to it.

Comparative Example 26

A copy test is made as in the same manner as described in Example 36, except that each of the developers of the above described developers for electrostatic latent image of C2, M2, Y2, and K2 of cyan, magenta, yellow and black is used as a developer, a non-coat paper for full-color printing having ten point average surface roughness Rz=13 μ m (whiteness degree: 84%) is used as a transfer material, the TMA value of a region having an image area rate of 100% of each single toner of (Image 1) of Example 36 on the transfer material is controlled to be a value shown in the following Table 14, and the developing conditions for each color toner of (Image 2) to (Image 4) are matched to it.

Comparative Example 27

A copy test is made as in the same manner as described in Example 36, except that each of the developers of the above described developers for electrostatic latent image of

C2, M2, Y2, and K2 of cyan, magenta, yellow and black is used as a developer, a coat paper for full-color printing having ten point average surface roughness $R_z=5\text{ }\mu\text{m}$ (whiteness degree: 80%) is used as a transfer material, the TMA value of a region having an image area rate of 100% of each single toner of (Image 1) of Example 36 on the transfer material is controlled to be a value shown in the following Table 14, and the developing conditions for each color toner of (Image 2) to (Image 4) are matched to it.

Comparative Example 28

A copy test is made as in the same manner as described in Example 36, except that an image forming device similar to Example 38 is used, a developer for surface-smoothing step (non-color and transparent) described in the Preparation of developer for surface-smoothing step is used as a developer for surface-smoothing step, each of the developers of the above described developers for electrostatic latent image of C2, M2, Y2 and K2 of cyan, magenta, yellow and black is used as a developer for image forming, a coat paper for full-color printing (ten point average surface roughness $R_z=9\text{ }\mu\text{m}$, whiteness degree: 80%) is used as a transfer material, the TMA value of a region having an image area rate of 100% of each single toner of (Image 1) of Example 36 on the transfer material is controlled to be a value shown in the following Table 14, and the developing conditions for each color toner of (Image 2) to (Image 4) are matched to it. The toner weight of the non-color transparent toner is 0.3 mg/cm^2 , and the ten point average surface roughness R_z after forming the layer is $6\text{ }\mu\text{m}$, and the whiteness degree is 80%.

TABLE 14

		TMA on a Region Having An Image Area Rate of 100% (mg/cm^2)			
		Cyan	Magenta	Yellow	Black
Example	36	0.25	0.26	0.30	0.25
	37	0.26	0.25	0.31	0.26
	38	0.23	0.27	0.32	0.26
	39	0.24	0.25	0.31	0.25
	40	0.31	0.31	0.40	0.33
Comparative Example	26	0.65	0.66	0.68	0.72
	27	0.60	0.63	0.62	0.71
	28	0.59	0.61	0.65	0.70

Methods and results of evaluation tests

The methods of evaluation tests in the copy tests in Examples 36 to 40 and Comparative Examples 26 to 28, are as follows:

Image Density

As to the solid image area having an image area rate of 100% obtained in (Image 1), the image density of the image area is determined with an X-Rite 404 (manufactured by X-Rite Co., Ltd.).

Minute line reproducibility evaluation test

At the time of image forming in (Image 1) and (Image 2), line images for cyan, magenta, yellow, black (single color), red, green, blue and process black are formed so as to have a line width of $50\text{ }\mu\text{m}$ on a photoconductor, and transferred to a transfer material and then fixed. The line image of the fixed image formed on the transfer material is observed using a VH-6220 Microhighscope (*KEYENCE* Co., Ltd.) at the magnification of 500. Evaluation is made with the criteria as shown below.

- : Center of minute lines is satisfactorily filled with toner and no disturbed edges are observed.

- △: Center of minute lines is satisfactorily filled with toner but jagged edges are observed.

- ×: Center of minute lines is not satisfactorily filled and jagged edges are observed to be very evident.

Gradation reproducibility evaluation test

At the time of image forming of (Image 3), the density of gradation image at in-put time and that of gradation image formed (out-put) on a transfer material are determined, and the variations of the gradation are evaluated. The image density is determined with a X-Rite 404 (manufactured by X-Rite Co., Ltd.). Evaluation is made with the criteria as shown below.

- : Both the gradation of the reproduced area and the gradation curve are satisfactory in the evaluation area.

- △: The gradation in the reproduced area is somewhat limited on a low-image area rate region and a high-image area rate region in the evaluation area.

- ×: The gradation in the reproduced range is limited on a low-image area rate region and a high-image area rate region in the evaluation area.

Graininess on highlight region

The gradation images having standards of 5% and 10% of image area rate of the gradation image obtained in (Image 3) are formed, the obtained images are observed visually, and the graininess on highlight region is evaluated. Evaluation is made with the criteria as shown below.

- : Graininess for 5% and 10% are very satisfactory.

- △: Graininess for 5% is somewhat unsatisfactory.

- ×: Graininess for 5% and 10% are unsatisfactory.

Color reproducibility evaluation test

As to each of the regions having image area rate of 100% of cyan, magenta, yellow and black (single color) and red, green, blue and process black for (Image 1) and (Image 2), the color reproducibility is determined with a 968 Spectrophotometer manufactured by X-rite Co., Ltd. Evaluation is made with the criteria as shown below.

- : Color reproducibility is satisfactory (having a color reproducibility equal to or higher than the color reproduced region by 175 line offset printing).

- △: Color reproducible range is somewhat limited (having a color reproducibility equal to the color reproduced region by 175 line offset printing).

- ×: Color reproducibility is unsatisfactory (the color reproduced region by 175 line offset printing can not be reproduced).

Image glossiness uniformity evaluation test

As to each of the images of (Image 1), (Image 2) and (Image 3), the difference between the image glossiness of a transfer material and the image region of tertiary color having image density of 1, 2 or more, and the difference between the image glossiness of the image region of the primary color having an image density of 1, 2 or more and the image glossiness of the image region of the tertiary color having an image density of 1, 2 or more, are evaluated organoleptically, respectively. Evaluation is made with the criteria as shown below.

- ◎: Image glossiness difference is low and satisfactory (which is almost equal to that of an image obtained by offset printing).

- : Image glossiness is slightly high but non-uniform impression is low.

- △: Image glossiness of the image region of tertiary color is too high and non-uniform image impression is felt, compared with an image obtained by offset printing.

- ×: Different image quality impression from an image obtained by offset printing is shown since the image glossiness difference in an image region is large.

Image quality evaluation test for picture image

As to the picture image obtained in (Image 4), a comparison of image quality with an image obtained by 175 line offset printing is made by an organoleptic evaluation. Evaluation is made with the criteria as shown below.

⊙: Image quality impression is equal to or higher than that of an image obtained by 175 line offset printing.

○: Image quality impression is slightly inferior to that of an image obtained by 175 line offset printing.

Δ: Image quality impression is inferior to that of an image obtained by 175 line offset printing.

×: Image quality impression is different from that of an image obtained by 175 line offset printing.

Image offset evaluation test

Image offset evaluation test is made using an apparatus so modified that a temperature setting of heating roll and pressure roll of A color 935 can be controlled optionally and the fixing temperature can be monitored. Concretely, at the time of image forming of (Image 3), an un-fixed image of a gradation image is formed, the temperature of the heating roll and the pressure roll is set at 160° C., the fixing speed is controlled to be the same as A color 935, and the evaluation of image offset is made. Evaluation is made with the criteria as shown below.

○: Offset does not occur.

Δ: Offset slightly occurs, but is cleaned sufficiently with a roll cleaning mechanism and is not transferred to the transfer material.

×: Offset occurs.

The results of the above evaluation tests are shown in the following Tables 15A and 15B.

With the method for forming an image according to the present invention, an image having no fogging can be formed, and minute line reproducibility and gradation are rendering satisfactory, a uniform image glossiness corresponding to the surface glossiness of a transfer material itself can be obtained, and image quality equal to or higher than an image formed by offset printing can be achieved, with a small-sized toner for developing an electrostatic latent image having a high transfer efficiency and an excellent durability.

In addition, with the method for forming an image according to the present invention, even with a transfer material having a rough surface state, the minute line reproducibility and gradation can be satisfactory and image quality equal to or higher than an image formed by offset printing can be achieved.

What is claimed is:

1. A toner for developing an electrostatic latent image comprising coloring particles containing a colorant and a binder resin, wherein a volume average particle size of the coloring particles is 1.0 to 5.0 μm , wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of 20% by number or less of a total number of coloring particles and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less of the total number of coloring particles, and wherein the colorant is a pigment.

2. A toner for developing an electrostatic latent image according to claim 1, wherein coloring particles having a particle size of 1.0 μm to 2.5 μm are present in an amount of 5% to 50% by number.

TABLE 15A

Example/ Comp. Ex.	Developer	Transfer				material Surface-smoothing process			
		Surface Rz	White- ness	Rz after treatment	White- ness	Image Density			
		(μm)	(%)			C	M	Y	K
Ex.	36	9	80	None	—	1.6	1.6	1.4	1.5
	37 C1	5	85	None	—	1.8	1.8	1.6	1.7
	38 M1	9	80	Non-color transparent	5	80	1.7	1.8	1.6
	Y1								
	39 K1	16	75	White	9	89	1.6	1.6	1.4
	40	16	75	None	—	—	1.4	1.4	1.3
Comp. Ex.	26 C2	9	80	None	—	—	1.7	1.8	1.7
Ex.	27 M2	5	85	None	—	—	1.8	1.9	1.6
	Y2								
	28 K2	9	80	Non-color transparent	5	80	1.8	1.8	1.6

TABLE 15B

Example/ Comp. Ex.	Minute Line Reproducibility	Gradation Reproducibility	Highlight Region Graininess	Color Reproducibility	Image Glossiness Uniformity	Image Quality of Picture	Image Offset
Ex.	36	○	○	○	○	○	○
Ex.	37	○	○	○	⊙	⊙	○
Ex.	38	○	○	○	⊙	⊙	○
Ex.	39	○	○	○	○	○	○
Ex.	40	○	○	○	Δ	Δ	Δ
Comp. Ex.	26	X	X	X	○	X	○
Comp. Ex.	27	X	X	X	○	X	○
Comp. Ex.	28	X	X	X	○	X	○

3. A toner for developing an electrostatic latent image according to claim 1, wherein coloring particles having a particle size of 4.0 μm or less are present in an amount of 75% by number or more.

4. A toner for developing an electrostatic latent image according to claim 1, wherein an average particle diameter of the pigment in the coloring particles is 0.3 μm or less.

5. A toner for developing an electrostatic latent image according to claim 1, wherein a q/d in a frequency distribution, at a temperature of 20° C. and a humidity of 50%, has a peak value of 1.0 or less and a bottom value of 0.005 or more, wherein q represents the electric charge quantity of said toner for developing electrostatic latent image in fC and d represents the volume average particle size of the coloring particles for developing electrostatic latent image in μm .

6. A toner for developing an electrostatic latent image according to claim 1, wherein a concentration of the pigment in the coloring particles, C (% by weight), a true specific gravity of the coloring particles, a (g/cm^3), and the volume average particle size of the coloring particles, D (μm), fulfill the relationship represented by the formula

$$25 \leq a \cdot D \cdot C \leq 90.$$

7. A toner for developing an electrostatic latent image comprising coloring particles containing a colorant and binder resin, wherein

(a) a volume average particle size of the coloring particles is 1.0 to 5.0 μm , and

(b) a q/d in a frequency distribution, at a temperature of 20° C. and a humidity of 50%, has a peak value of 1.0 or less and a bottom value of 0.005 or more, wherein q represents the electric charge quantity of said toner for developing electrostatic latent image in fC and d represents the volume average particle size of the coloring particles for developing electrostatic latent image in μm .

8. A toner for developing an electrostatic latent image according to claim 7, wherein the peak value of q/d in a frequency distribution is 0.80 or less.

9. A toner for developing an electrostatic latent image according to claim 7, wherein the bottom value of q/d in a frequency distribution is 0.01 or more.

10. A toner for developing an electrostatic latent image according to claim 7, wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of 20% by number or less of a total number of coloring particles, and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less of the total number of coloring particles.

11. A toner for developing an electrostatic latent image according to claim 7, wherein an aggregation degree of the toner for developing an electrostatic latent image is 30 or less.

12. A toner for developing an electrostatic latent image according to claim 7, wherein the toner further comprises an external additive, and wherein

(a) the external additive comprises at least one type of ultra microparticles having an average primary particle size of 30 nm to 200 nm and at least one type of super-ultra microparticles having an average primary particle size of 5 nm or more and less than 30 nm, and

(b) coating rates, Fa and Fb, of the external additive based on a surface of the coloring particles obtained according to Formula (1)

$$F = \sqrt{3} \cdot D \cdot \rho_c \cdot (2\pi r \rho_o)^{-1} \cdot C \times 100 \quad (1)$$

wherein F denotes a coating rate (%), D denotes the volume average particle size of the coloring particles (μm), ρ_c denotes a true specific gravity of the coloring particles, z denotes an average primary particle size of the additive, ρ_o denotes the true specific gravity of an additive, and C denotes the ratio (x/y) of the weight of the additive, x (g), to the weight of the coloring particles, y (g),

for the ultra microparticles and the super-ultra microparticles, respectively, are both 20% or more, and the total of the coating rate of the entire additive is 100% or less.

13. A toner for developing an electrostatic latent image comprising coloring particles containing a colorant and binder resin, and an external additive, wherein

(a) a volume average particle size of the coloring particles is 1.0 to 5.0 μm , and wherein coloring particles having a particle size of 1.0 μm or less are present in an amount of 20% by number or less of a total number of coloring particles, and coloring particles having a particle size exceeding 5.0 μm are present in an amount of 10% by number or less of the total number of coloring particles,

(b) the external additive comprises at least one type of ultra microparticles having an average primary particle size of 30 nm to 200 nm and at least one type of super-ultra microparticles having an average primary particle size of 5 nm or more and less than 30 nm, and

(c) coating rates, Fa and Fb, of the external additive based on a surface of the coloring particles obtained according to Formula (1)

$$F = \sqrt{3} \cdot D \cdot \rho_c \cdot (2\pi r \rho_o)^{-1} \cdot C \times 100 \quad (1)$$

wherein F denotes a coating rate (%), D denotes the volume average particle size of the coloring particles (μm), ρ_c denotes a true specific gravity of the coloring particles, z denotes an average primary particle size of the additive, ρ_o denotes the true specific gravity of an additive, and C denotes the ratio (x/y) of the weight of the additive, x (g), to the weight of the coloring particles, y (g),

for the ultra microparticles and the super-ultra microparticles, respectively, are both 20% or more, and the total of the coating rate of the entire additive is 100% or less.

14. A toner for developing an electrostatic latent image according to claim 13, wherein the coating rate of the ultra microparticles, Fa (%), and the coating rate of the super-ultra microparticles, Fb (%), are satisfy $0.5 \leq Fb/Fa \leq 4.0$.

15. A toner for developing an electrostatic latent image according to claim 13, wherein 75% by number of the total number of coloring particles have a particle size of 4.0 μm or less.

16. A toner for developing an electrostatic latent image according to claim 13, wherein the at least one type of ultra microparticles are silicon oxide microparticles imparted with hydrophobicity.

17. A toner for developing an electrostatic latent image according to claim 13, wherein the at least one type of super-ultra microparticles are titanium compound microparticles.

18. A toner for developing an electrostatic latent image according to claim 13, wherein a q/d in a frequency distribution, at a temperature of 20° C. and a humidity of 50%, has a peak value of 1.0 or less and a bottom value of 0.005 or more, wherein q represents the electric charge quantity of said toner for developing electrostatic latent image in fC and d represents the volume average particle size of the coloring particles for developing electrostatic latent image in μm .

19. A developer for an electrostatic latent image comprising at least a carrier and the toner of claim 1.

20. A developer for an electrostatic latent image comprising at least a carrier and the toner of claim 7.

21. A developer for an electrostatic latent image comprising at least a carrier and the toner of claim 13.

22. A method for forming an image comprising forming an electrostatic latent image on a latent image support, forming a toner layer comprised of toner on a surface of a developer that is arranged opposed to the latent image support,

developing the electrostatic latent image on the latent image support with said toner layer to form a toner image, and

transferring the toner image developed onto a transfer material, wherein said toner comprises the toner of claim 1.

23. A method for forming an image according to claim 22, wherein a ten-point average surface roughness R_z of at least an image-receiving region of the transfer material is 10 μm or less.

24. A method for forming an image according to claim 22, wherein the method further comprises smoothing at least the image-receiving region of a surface of the transfer material before transferring the toner image to the surface of the transfer material.

25. A method for forming an image according to claim 24, wherein a ten point average smooth roughness R_z of at least the image-receiving region of the surface of the transfer material is 10 μm or less following the smoothing.

26. A method for forming an image according to claim 24, wherein the smoothing comprises forming a layer comprising a non-color transparent toner on at least the image-receiving region of the transfer material.

27. A method for forming an image according to claim 24, wherein the smoothing comprises forming a layer comprising a white toner on at least the image-receiving region of the transfer material.

28. A method for forming an image according to claim 22, wherein coloring particles having a size of 1.0 to 2.5 μm comprise from 5 to 50% by number of the total number of coloring particles in the toner.

29. A method for forming an image according to claim 22, wherein the toner is a color toner.

30. A method for forming an image according to claim 22, wherein a toner weight per one color of the toner image transferred onto a transfer material is 0.40 mg/cm² or less.

31. A method for forming an image according to claim 22, wherein the method further comprises forming a full color image by overlaying sequentially in any order toner images of at least three colors including cyan, magenta and yellow onto the transfer material.

32. A method for forming an image comprising forming an electrostatic latent image on a latent image support,

forming a toner layer on a surface of a developer support which faces the latent image support,

developing the electrostatic latent image on the latent image support with said toner layer to form a toner image, and

transferring the toner image developed onto a transfer material,

wherein said toner comprises the toner of claim 7.

33. A method for forming an image according to claim 32, wherein the method further comprises forming a full color image by overlaying sequentially in any order toner images of at least three colors including cyan, magenta and yellow onto the transfer material.

34. A method for forming an image according to claim 32, wherein a ten-point average surface roughness R_z of at least an image-receiving region of the transfer material is 10 μm or less.

35. A method for forming an image comprising forming an electrostatic latent image on a latent image support,

forming a toner layer on a surface of a developer support which faces the latent image support,

developing the electrostatic latent image on the latent image support with said toner layer to form a toner image, and

transferring the toner image developed onto a transfer material,

wherein said toner comprises the toner of claim 13.

36. A method for forming an image according to claim 35, wherein the method further comprises forming a full color image by overlaying sequentially in any order toner images of at least three colors including cyan, magenta and yellow onto the transfer material.

37. A method for forming an image according to claim 35, wherein a ten-point average surface roughness R_z of at least an image-receiving region of the transfer material is 10 μm or less.

* * * * *

POWDER CHARACTERISTICS TESTER

OPERATING INSTRUCTIONS

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Madison, New Jersey 07940-0575
(201) 966-1245

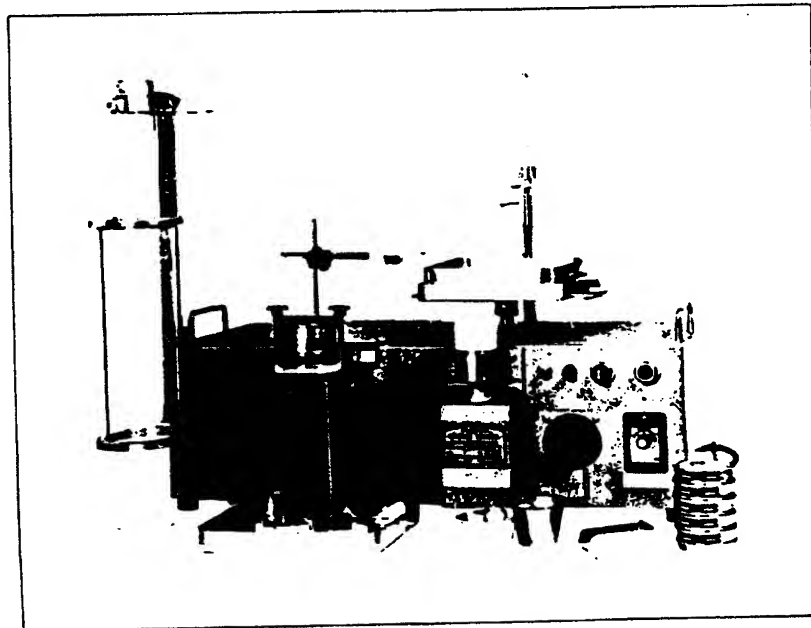
HOSOKAWA IRON WORKS, LTD.
OSAKA, JAPAN.

1. INTRODUCTION

The Hosokawa Micromeritics Laboratory has designed the Powder Tester based upon research performed and published by Mr. Ralph L. Carr, Jr., Chief Chemist of B I F, a Unit of General Signal Corporation, Providence, Rhode Island, U.S.A. Recognizing that the work of Mr. Carr was of great importance in the field of powder processing and handling the Hosokawa Micromeritics Laboratory designed the Powder Tester as a rapid aid to the chemist, chemical engineer or technologist dealing with powders for quickly arriving at the "flowability index" for any powder; thus providing the design engineer with a maximum of useful information for designing the most efficient powder handling equipment.

The Powder Tester has been designed to do mechanically many of the routines previously done manually. While it is recognized that experience will permit a trained person to arrive at comparatively constant results in performing certain manual operations there are many human factors that can produce misleading results. Such things as nervous tension, impatience, fatigue, a common cold and many other human ailments can be the cause of inaccuracy in performing a manual procedure. With the Powder Tester the human factors mentioned are eliminated. The unit is designed to perform in the same manner without variation the various procedures set forth by Mr. Carr. By controlled mechanical means a more consistent and accurate "flowability index" can be determined than by manual methods.

Few, if any, liberties have been taken with Mr. Carr's research except that the various measurements done by Mr. Carr have been converted to the metric system. Certain information contained herein has been used with the permission of Mr. Carr, and the copyright owner, McGraw-Hill Inc., New York, N.Y. 100036, U.S.A. It is recommended that the original works of Mr. Carr, published in the McGraw-Hill "Chemical Engineering" magazine issue of Jan. 18, 1965, be studied carefully; its through study will help the operator master the simple use and technicalities of the Powder Tester. Being familiar with Mr. Carr's work will enable the operator to quickly arrive at the mathematical answers to the problems of Powder Flowability.



2. UNPACKING THE CASE

When the case is unpacked, the following items should be contained therein:

1. Main machine (Please refer to the drawing, photo 1)
2. Spatula assembly (Photo 2)
3. Dispersibility measuring unit (Photo 3)
4. Attachments, 25 pcs. including Parts Box (Photo 4)
5. Operating Instruction booklet.

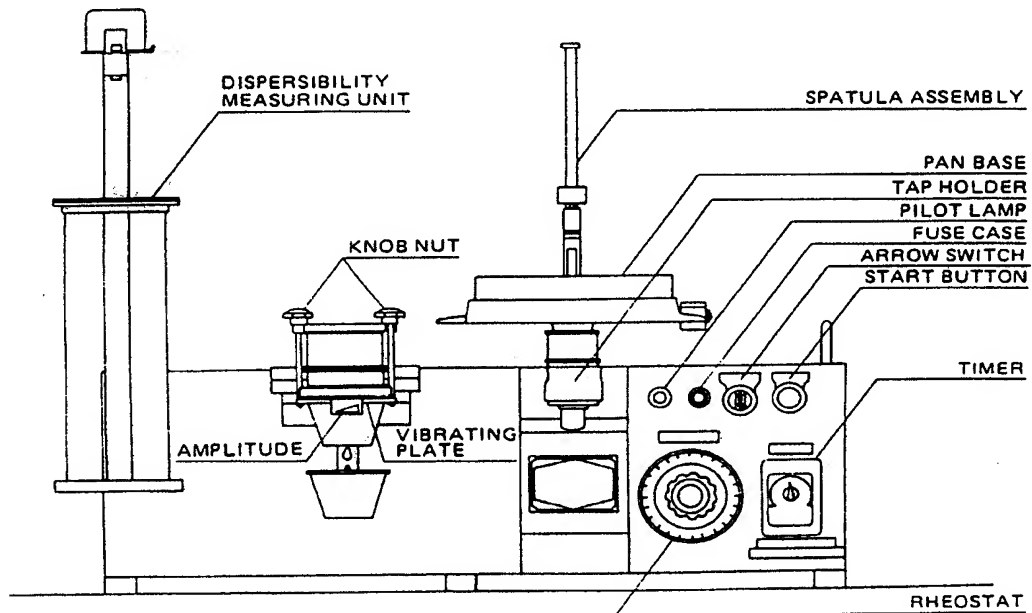


Photo 1

2) Spatula Assembly (Photo 2)

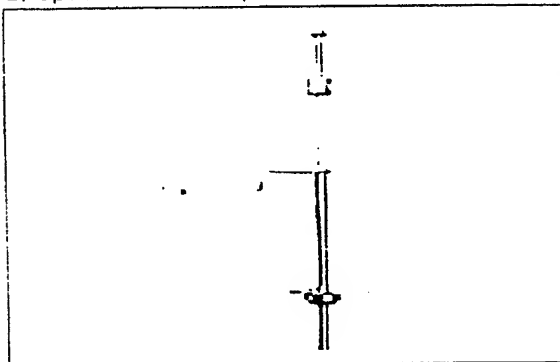


Photo 2

3) Dispersibility Measuring Unit (Photo 3)

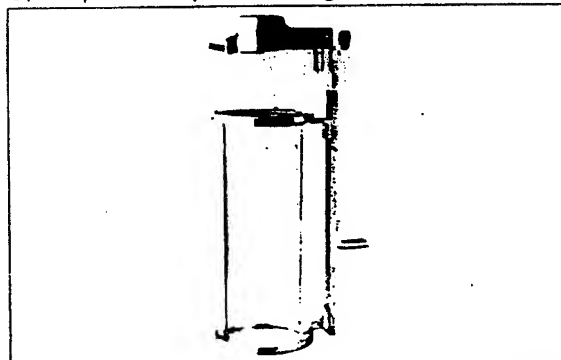
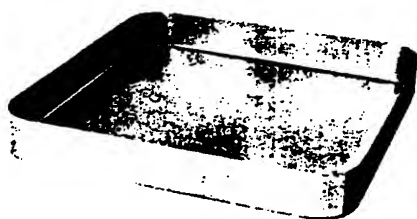


Photo 3

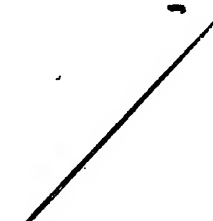
4) Attachments (25 pieces) (Photo 4)



① Square Pan



② Scoop



③ Scraper



④ Watch Glass (2 pcs.)
(1 pce. for spare)

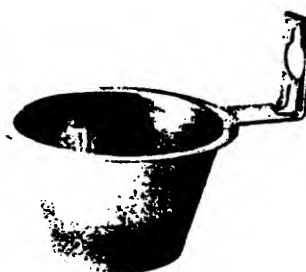
⑤ Cup Extension Piece



⑥ Cup (for bulk density)



⑦ Guide (2 pcs.)
(1 pce. for spare)



⑧ Stationary Chute



⑨ Vibrating Chute



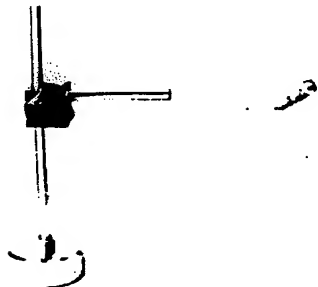
⑩ Screen
(#24, 42, 60,
(100, 200,)
(350 1 each)



⑪ Screen Cover

⑫ Space Ring

⑬ Screen Holding Bar



⑮ Protractor Stand



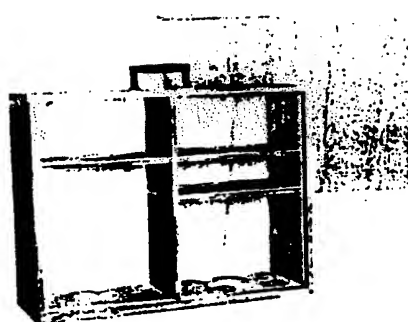
⑰ Shocker



⑭ Pan



⑯ Platform

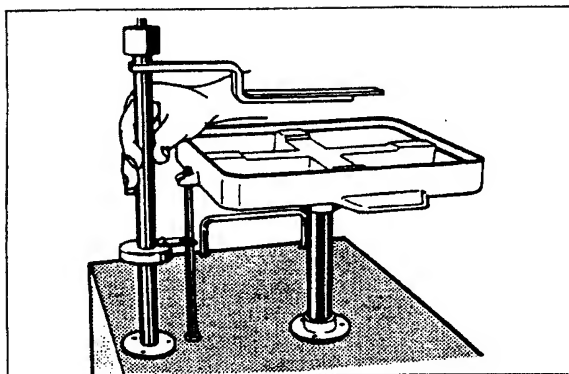


⑱ Parts Box

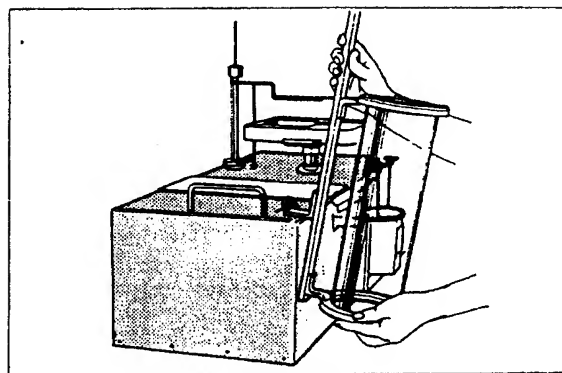
Photo 4

3. PREPARATION FOR USE:

1. Place the Powder tester on a strong bench or work table. If possible, use a concrete or ceramic table. If the table is not rigid the vibration of the machine will result in non-stable data.
2. Insert the Spatula Assembly in the hole at the top of the main body so that the spatula points to the front of the machine. Please refer to Sketch 5. Ascertain that the positioning pin sets firmly into the hole of the Spatula's pole collar.
3. Place the square pan (1) on to main machine where the spatula is in place.



Sketch 5



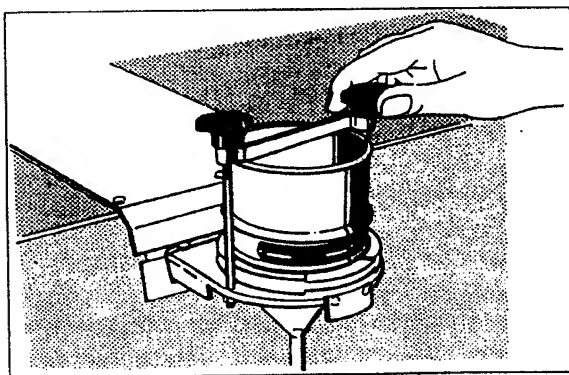
Sketch 6

4. Place the dispersibility measuring unit as shown in Sketch 6. (This unit may be placed for use only when required)
5. Connect the input power supply plug to the rated electricity outlet.
6. Insure that the pilot lamp is lit. If the lamp is not lit, check the fuse case, and replace fuse if necessary.
7. When preparation is completed the machine is ready for operation.

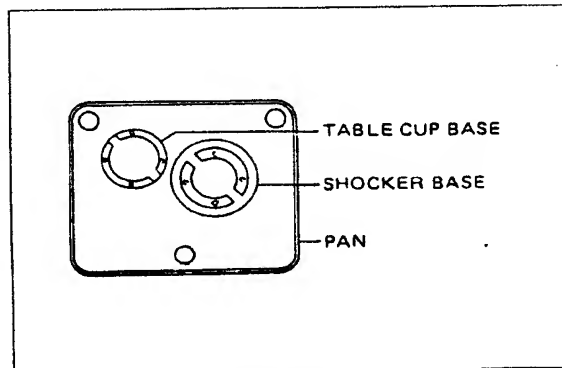
4. ANGLE OF REPOSE, ANGLE OF FALL AND ANGLE OF DIFFERENCE

4-1 Angle of Repose:

1. Remove funnel shaped guide (7) and the 24 mesh screen (10) from the vibrating unit holder, set the white plastic ring (12) on top of the glass funnel and then replace the 24 mesh screen and container. Place the screen holding bar and tighten the screw knobs. (Please refer to Sketch 7).
2. Place the round platform (16) in its base on the tray and carefully center under the glass funnel. (See Sketch 8).

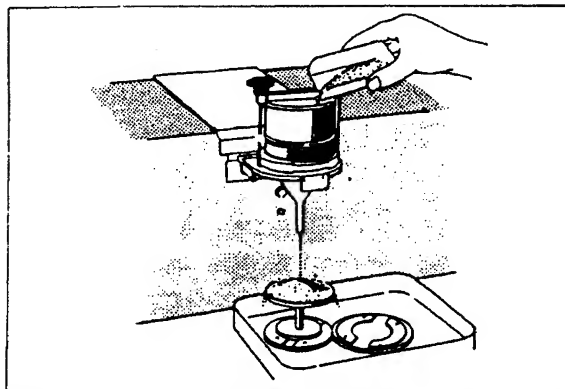


Sketch 7



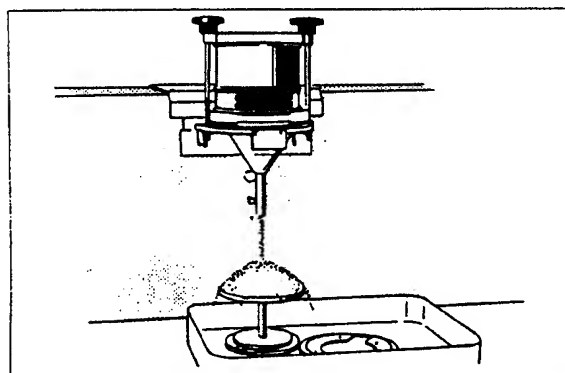
Sketch 8

3. Using scoop (2), fill the container with the powder to be measured. Please refer to Sketch 9.



Sketch 9

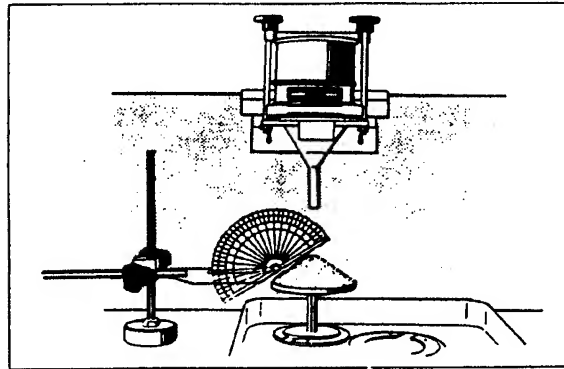
4. Reset the arrow switch to "VIB" and set the timer switch to full length. (180 seconds on 60 cycle supply).
5. Ascertain that the rheostat is set at "0".
6. Push the "START" button.
7. Increase the voltage on the rheostat and let the powder flow out of the end of the glass funnel and build up on the round platform in a conical shape. Amplitude of vibrating plate should not exceed 2mm, as indicated on the vibration scale. The powder should be allowed to overflow the platform and on to the tray and when the round platform is completely covered with powder and a cone shape has built up the unit either may be stopped by returning the rheostat to "0" or the unit will stop automatically when the timer switch reaches the "0" position. Please refer to Sketch 10.



Sketch 10

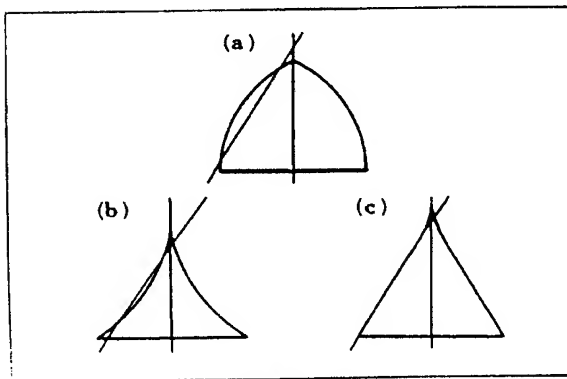
NOTE: After the initial vibration is set it may be necessary to reduce the vibration amplitude in the event the powder is flowing too fast to build up to a cone shape. Vibration amplitude may be reduced by simply turning the rheostat back towards the "0" position.

8. In case a conical shape is not completely formed repeat the above.
9. In the event the vibration has to be stopped during the operation the arrow switch should be returned to "OFF" position. Please do not re-set the rheostat while the timer switch is "ON".
10. After the cone has been built up, very carefully use the protractor on its stand (15) to measure the angle of the cone in relation to the edge of the platform. Please refer to Sketch 11.

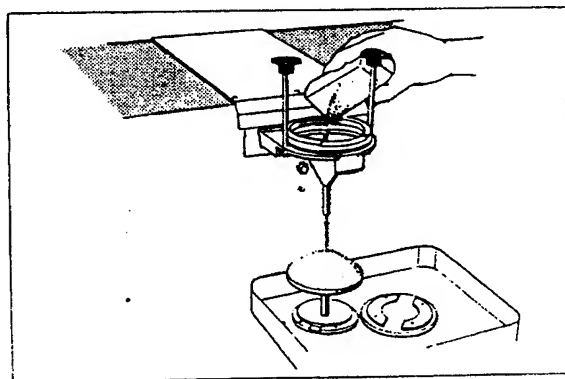


Sketch 11

11. Care, in the following should be exercised in testing.
 - a. Vibrating plate is balanced with the funnel and other attachments. Do not operate the vibrating plate by itself. If the vibrating plate is actuated without the attachments, it will produce an impingement sound even as low as at 1mm amplitude.
 - b. If the powder is fine and has a cohesive characteristic and the cone is irregular in shape measure several places and obtain an average figure or repeat the test three times and obtain an average.
 - c. When a slope of the cone becomes a curved line then an average angle should be read. Please refer to Sketch 12.
 - d. If the powder has a free-flowing characteristic or has coarse particles of larger than 24 mesh, the vibration is not necessary. So please remove screen (10) and charge the powder directly to the funnel by the scoop. (See Sketch 13)



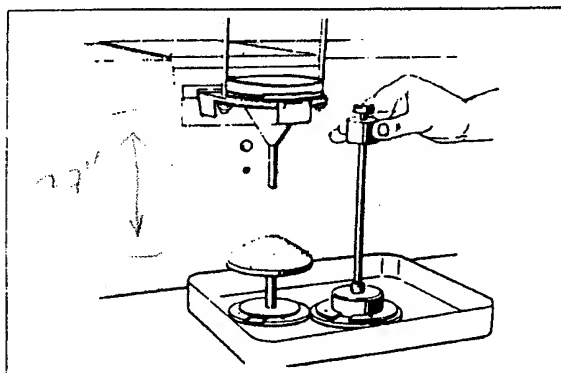
Sketch 12



Sketch 13

4-2 Angle of Fall:

1. After the determination of the Angle of Repose, place the shocker 17 on the shocker base (See Sketch 8)
2. Then raise the weight (carefully so that the cone will not be disturbed) on the slide and let it fall. Repeat this 3 times.



Sketch 14

3. Then measure the angle as before. Generally the Angle of Fall is smaller than the Angle of Repose.
4. Meaning of the Angle of Fall:
When the angle of Fall is small, the material has a free flowing characteristic. At the time when the angle falls, two phenomena are observed. In one case the particle falls along side of the cone's slope. In the other case the cone as a whole falls down. The latter phenomena is of special interest because it happens when the powder contains air within the powder layers. Such material often creates a flushing problem.

4-3 Angle of Difference:

The difference between the Angle of Repose and the Angle of Fall is defined as the Angle of Difference. The material has a characteristic of flushing when its Angle of Difference is great.

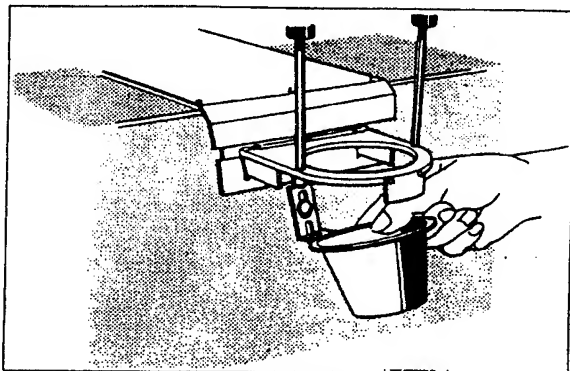
5. AERATED BULK DENSITY, PACKED BULK DENSITY AND COMPRESSIBILITY

5-1 Aerated Bulk Density:

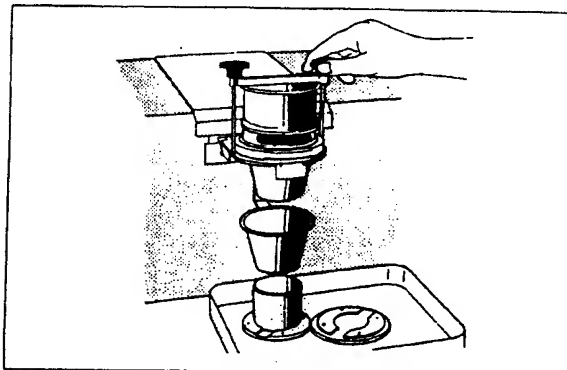
1. Fix the various attachments in the following order.
 - (i) Place the stationary chute (8) on the pins at the front of the tester. (Please refer to Sketch 15)
 - (ii) The following parts should be mounted on the vibrating plate.

Vibrating chute	(9)
Spacer ring	(12)
Screen (24 mesh)	(10)
Screen cover	(11)
Screen holding bar	(13)

As has been done with for the Angle of Repose, fasten the above parts by knob-nuts. (Please refer to Sketch 16)

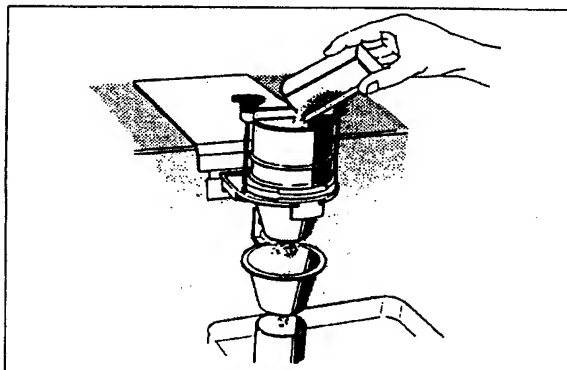


Sketch 15

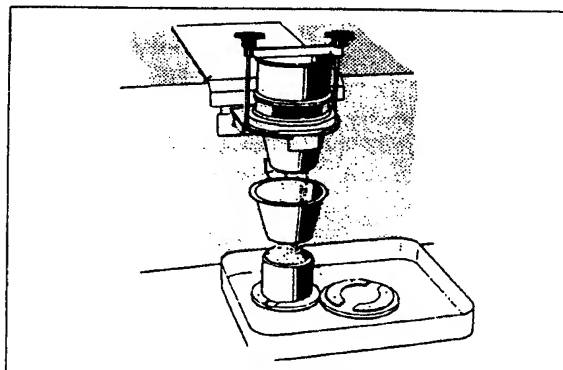


Sketch 16

2. Place the pan (14) directly under the stationary chute (8) and set in place bulk density measuring cup (6). The cup (6) should be inserted in the pit which is made in the pan (14). Make sure the center of the measuring cup (6) is in alignment with the center of the stationary chute (8). Please refer to Sketch 8.
3. Using scoop (2) gently put an adequate amount of the powder onto the screen (10).



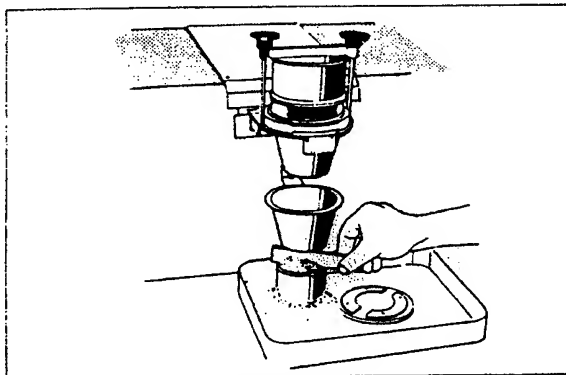
Sketch 17



Sketch 18

4. Set the selector switch to "VIB"
5. The timer should be set for the maximum.
6. Ascertain the vibration amplitude rheostat is set at the "0" position.
7. Push the start button.
8. Increase the voltage on rheostat. The powder flow rate is controlled by the rheostat. As a standard, set the rheostat so that it will require approximately 20-30 seconds to heap the powder above the edge of cup (6). If the cup is filled too slowly or too quickly then the results may vary considerably.
9. When the powder heaps up in the cup (6) return the rheostat dial to "0" and then stop the vibration.
10. Using the scraper carefully remove the powder mound from the cup (6) by drawing scraper (3) across the top of the container. This should be done carefully in order to leave a flat surface of powder which is exactly level with the edge of the cup (6). When drawing the scraper across the cup be sure to have the scraper in an exactly

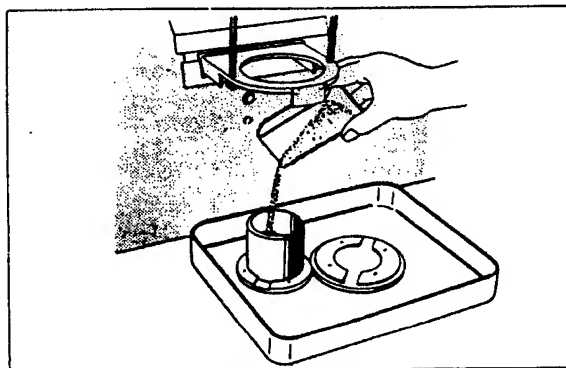
vertical position. When this has been done, weigh the container of powder carefully. The difference between the empty container weight and when full of powder will be the Bulk Density of the powder in grams per cc. (Note: as the container is exactly 100cc in volume the powder weight should be divided by 100 to arrive at gms/cc)



Sketch 19

11. Measure aerated bulk density 3 – 5 times and obtain an average figure.

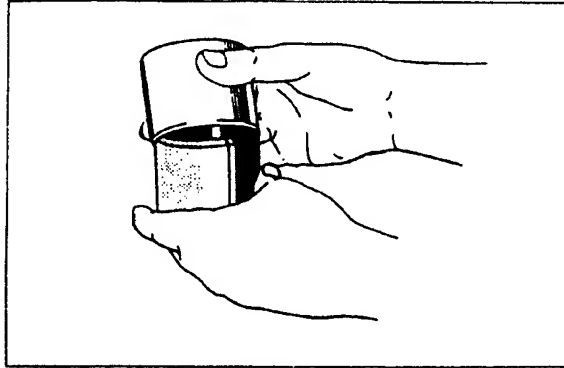
Note: When the powder is free-flowing and of fairly coarse particle size, it will not be necessary to pass the vibrating screen. The powder can be gently poured into the cup (6) by the scoop.



Sketch 20

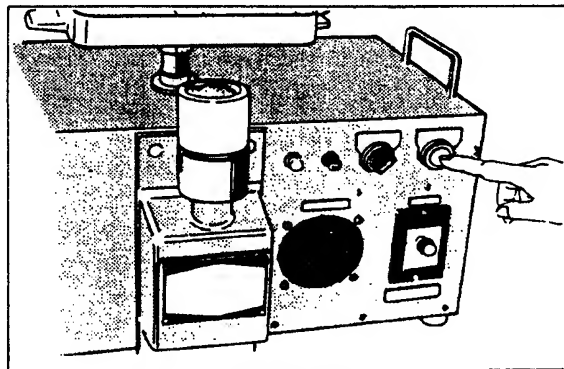
5-2 Packed Bulk Density.

1. Place the previously filled and leveled cup (6) in the automatic tapping device and place the cup extension piece (5) on top of the cup (6).



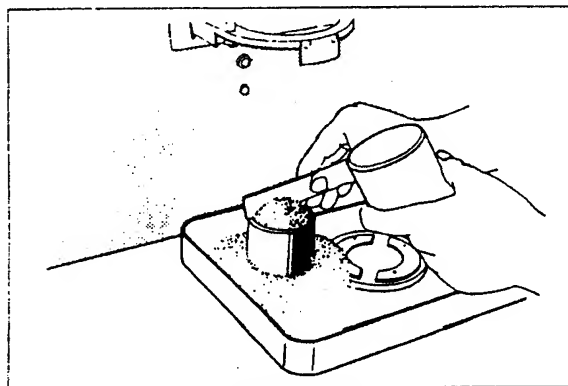
Sketch 21

2. Using the scoop (2) fill to the top with the same powder.
3. Turn the selector switch to the "TAP" position.
4. Set the timer switch at 180 seconds for 60 cycle. (For 50 cycle set the timer at 216 seconds)
5. Push the start button, which will activate the tapping device.



Sketch 22

6. During the tapping period it is necessary to observe the level of the powder and if necessary add powder to the container extension so that the powder will not pack below the rim of the container.
7. Tapping will be made 180 times and when the timer switch returns to the "0" position the tapping will cease automatically.
8. When the tapping is finished, remove the container and its extension (5). With the scraper remove the powder which is above the edge of the container. Use the same care when leveling off the container as in 5 - 1.



Sketch 23

9. Weigh the container and the powder and the difference in the weight of the empty container and when filled with powder will be the Packed Bulk Density (Divide the weight of powder by 100 to find the Packed Bulk Density in gms/cc)

Note: If the tapping will have to be stopped during the tapping period, change the selector switch to "OFF" then the tapping will be stopped.

5-3 Compressibility:

Compressibility C is calculated by the following equation (1) where the Aerated Bulk Density is expressed as A and the Packed Density is expressed as P.

$$C = 100 (P - A)/P \quad (\%) \text{ --- (1)}$$

Meaning of Compressibility:

The compressibility is a very important factor in finding the flow characteristic of a powder. When the compressibility is above 20%, the powder is not free-flowing and has a tendency for creating bridges in the hopper. In particular when the compressibility is 40 – 50%, it is very hard to discharge the material from the hopper once the material has been stored in it.

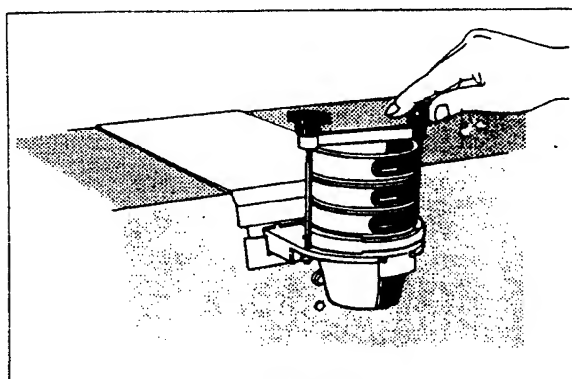
6. MEASURING THE COHESION

1. Place following parts onto the vibrating plate:

- (i) Vibrating chute (9).
- (ii) Spacer ring (12).
- (iii) Screen (200 mesh)
- (iv.) Screen (100 mesh)
- (v) Screen (60 mesh)
- (vi) Holding bar (13)

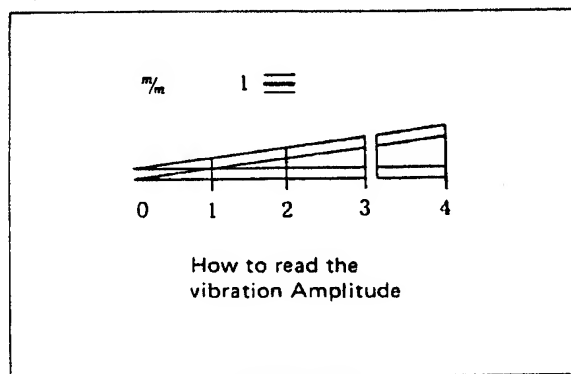
These screens should be used with the powder having the average bulk density of 0.4-0.9 gm/cc and all passing 200 mesh screen. Average bulk density = $\frac{A+P}{2}$

2. Fasten above parts by knob-nuts.



Sketch 24

3. Set the selector switch to "VIB".
4. Push the start button which will activate the vibration. Set the rheostat so that the vibration amplitude will be 1mm. The amplitude is read on the amplitude gauge. Please refer to the Sketch 25 which shows the amplitude of 1mm. The vibrating plate is supported by the cushion rubber so that in the very beginning vibration may be a bit unstable.



Sketch 25

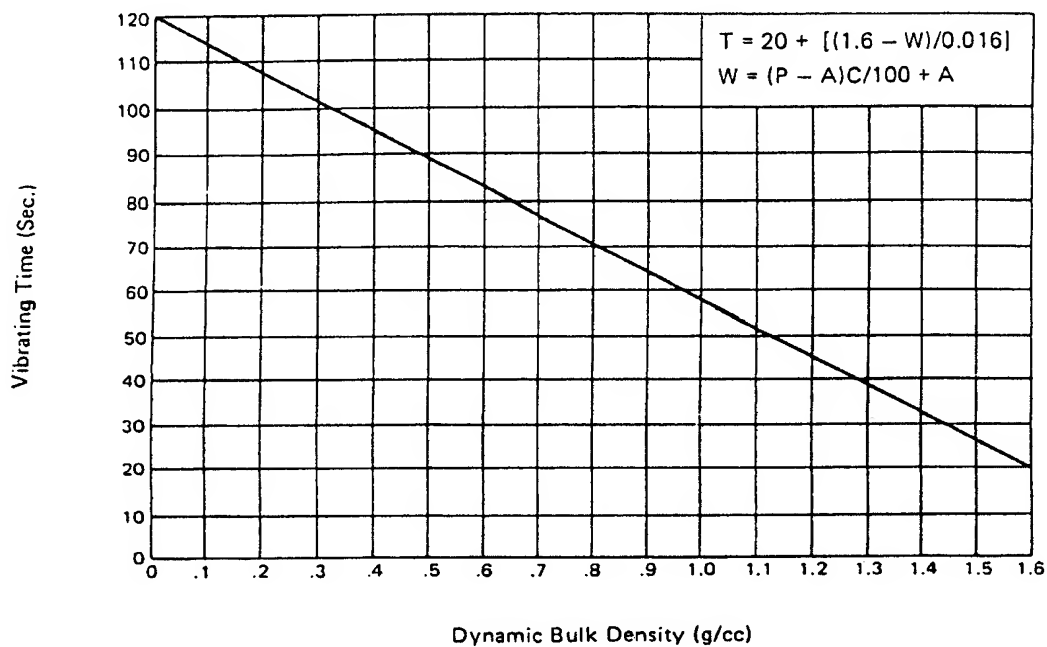
5. Wait until the timer comes to stop.
6. Set the timer according to the vibrating time calculated by the equation (2) and (3).

$$T = 20 + ((1.6 - W)/0.016) \dots \dots \text{(Seconds)} \dots (2)$$

$$W = (P - A) C/100 + A \dots \dots \dots \text{(g/cc)} \dots \dots (3)$$

Where P Packed Bulk Density
 A Aerated Bulk Density
 C Compressibility
 W Dynamic Bulk Density

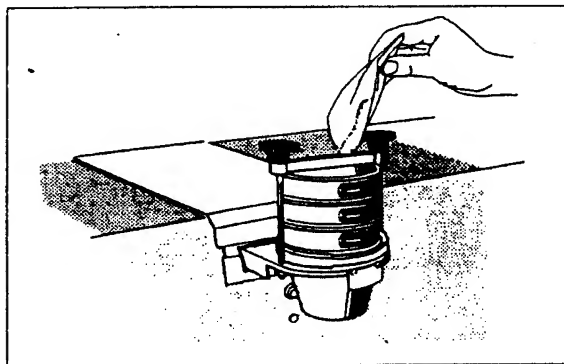
The relationship between T and W is shown in the Sketch 26. The graduation of the timer is by 5 seconds and it is not sufficiently accurate for this purpose. Thus the timer should be adjusted against a stopwatch so that the vibration will be given for the period calculated by the equation (2).



Sketch 26

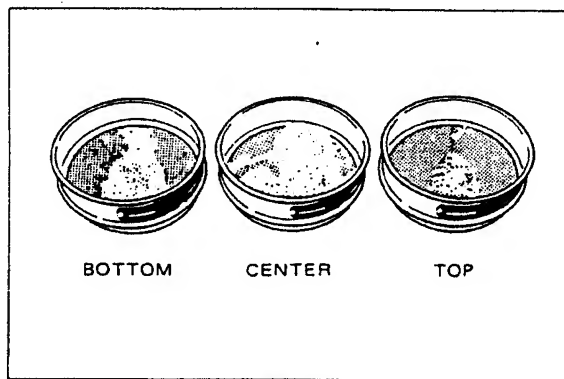
Relationship between T and W
 $T = 20$ sec. for the $W = 1.6$ gr/cc or more

7. While adjusting the timer, at the same time, the rheostat also should be re-adjusted to give an amplitude of 1mm.
8. Wait until the timer comes to a complete stop.
9. Weigh 2 gms. of powder and place it on the screen.



Sketch 27

10. Push the start button.
11. When vibration stops, loosen the knob nuts and remove the 3 screens and weigh the amount of powder retained on each screen. Brush off all material from the screen.



Sketch 28

12. Cohesion is calculated by following method.

$$\frac{\text{Material retained on the top screen}}{2g} \times 100 \dots (4) a$$

$$\frac{\text{Material retained on the center screen}}{2g} \times 100 \times \frac{3}{5} \dots (4) b$$

$$\frac{\text{Material retained on the bottom screen}}{2g} \times 100 \times \frac{1}{5} \dots (4) c$$

Sum of above three figure (4) a, (4) b and (4) c will give the Cohesion (%).

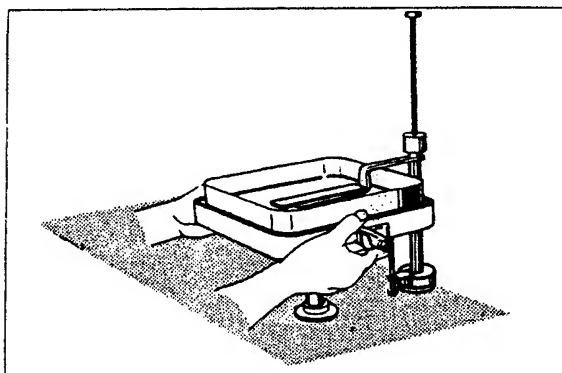
Meaning of Cohesion:

The powder has lesser flowability when it has a higher Cohesion %. With powder which has higher Cohesion, care is needed in designing feeder, hopper and other handling equipment.

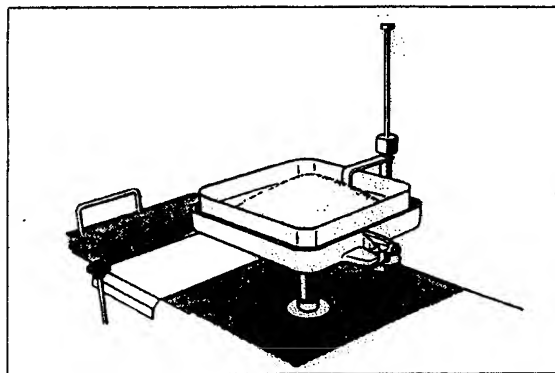
- Note:
1. With comparatively light material (i.e. Average bulk density = 0.16 – 0.4g/cc) use coarse screen (i.e. 42, 60, 100 mesh). For heavier material (i.e. average bulk density = 0.9 – 1.5g/cc) use fine screens (i.e. 100, 200, 350 mesh). In any case the material should be fine enough to pass the bottom screen.
 2. If the material particles have a tendency to be attracted to each other by electrostatic force or form balls on vibration, accurate figures cannot be obtained.
 3. Measuring can be done using either 50 or 60 cycle current but use the same cycle for comparison purposes.

7. MEASURING ANGLE OF SPATURA

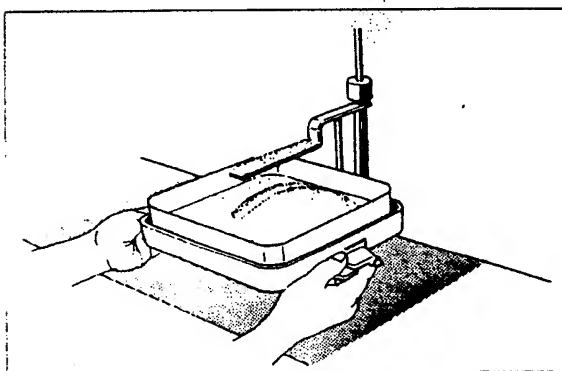
1. Raise the pan on top of the Powder Tester until the pan touches the spatula. Use both hands to lift the pan. (See Sketch 29)
2. Fill the pan with the powder so that the spatula is completely covered with several centimeters of powder. (See Sketch 30)
3. Carefully lower the pan which will expose the spatula with a considerable quantity of powder on it. (See Sketch 31).
4. Carefully measure the Angle of the Powder on the spatula and if the appearance of the powder is irregular then measure the angle at several different points and obtain the average. (See Sketch 32)



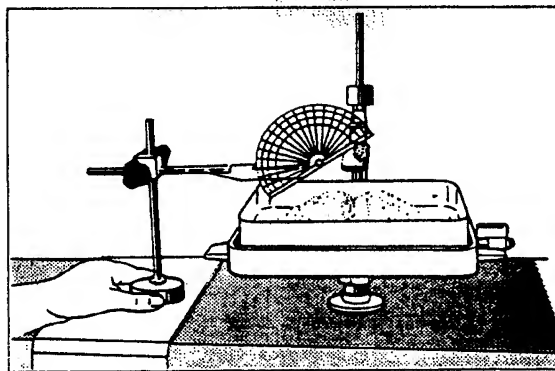
Sketch 29



Sketch 30

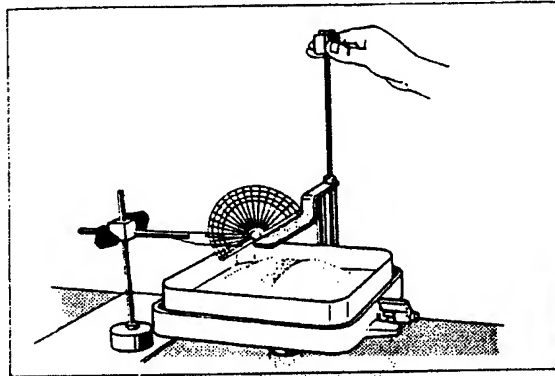


Sketch 31



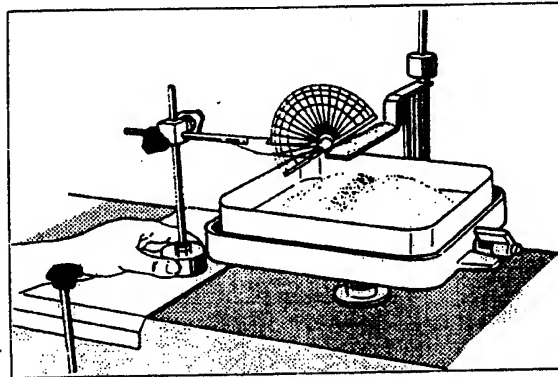
Sketch 32

5. Raise the weight of the slide hammer and let it fall once. (See Sketch 33)



Sketch 33

6. Then measure the angle after dropping the slide hammer.



Sketch 34

7. If necessary measure the angle at several points and obtain the average. Add 2 average angles (i.e. before and after dropping the hammer) and divide by 2 which will give the Angle of Spatula.

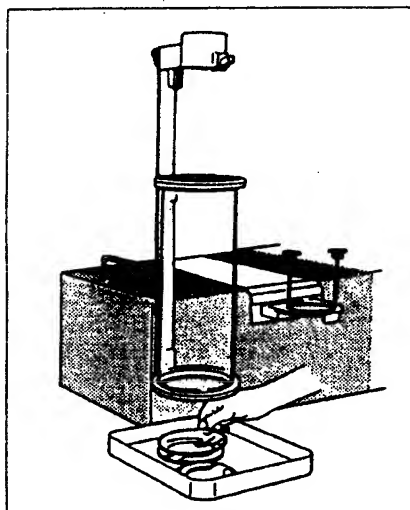
Meaning of Angle of Spatula:

The higher the Angle of Spatula, the worse the flowability of powder is. The Angle of Spatula is always greater when the Angle of Repose.

Note: When heaping up the powder on the spatula, use approximately the same amount always, otherwise the figure will fluctuate and cannot be compared from one to the other.

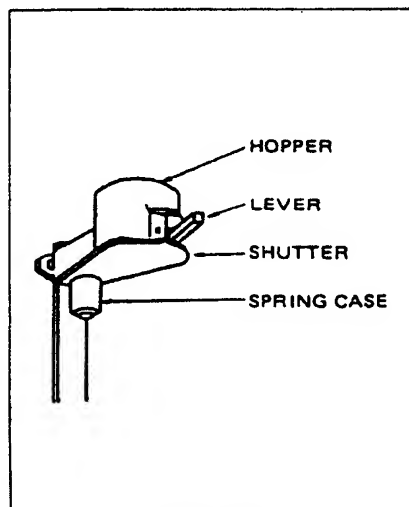
8. DISPERSIBILITY

1. As explained in the preparation, set the Dispersibility Measuring unit in place.
2. Place the pan (14) under the cylindrical glass tube. Put the spacer ring (12) into the pit of the pan (14) and then place the watch glass in position.
3. Center the watch glass (4) carefully under the glass tube.



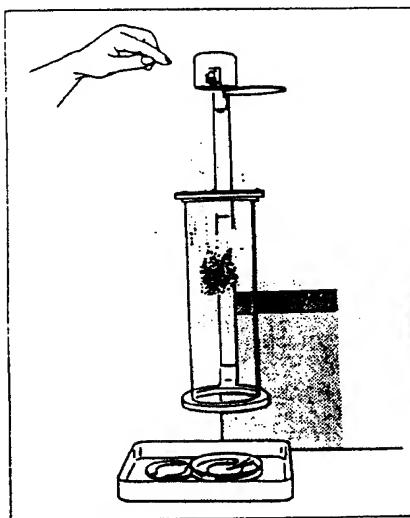
Sketch 35

4. Carefully weigh 10 grams of powder and place it in the container which is above the round glass tube. (Please refer to Sketch 36)



Sketch 36

5. Push lever down which will cause the damper at the bottom of the container to spring to one side allowing the powder to fall through the glass tube and onto the watch glass.



Sketch 37

6. Weigh the watch glass and the powder.

Note: Weigh the watch glass before the start of this test.

7. Dispersibility is obtained by the following equation.

$$(10 - \text{Weight of powder on watch glass}) \times 10 = \% \text{ of Dispersibility} \dots\dots (5)$$

Meaning of Dispersibility:

Dispersibility indicates the fugacity, dusting and flushing characteristics of powder. If the dispersibility index is higher than 50%, the powder will have a high flushing characteristic.

Note: When the damper does not spring well, pull down the spring case which is placed underneath the damper, and re-set the spring in the following manner: Detach the hook and wind the spring by turning it in an anticlockwise direction. There are four hook holes positioned every 90 degrees, so replace the hook in the proper hole.

9. NUMERICAL EVALUATION SYSTEM OF FLOWABILITY AND FLOODABILITY:

All of the figures measured in the foregoing have a meaning in themselves as the physical properties of the powder. Mr. Carr has tried to evaluate powder's flowability and floodability in a numerical manner with a combination of these various physical characteristics. For this purpose Mr. Carr has published tables for the conversion of the measured figures into a common index. To use the figures obtained with the Powder Tester as if they are in direct relationship with Mr. Carr's tables may not be appropriate. However, the Powder Tester will be a useful and practical aid for the comparison of the properties of the same powders.

9-1 Evaluation System of Flowability

The four characteristics mentioned below are utilized for numerical evaluation of Flowability

1. Angle of Repose
2. Compressibility
3. Angle of Spatula
4. Cohesion or Uniformity

Uniformity is the index to indicate the range of the particle size distribution. This uniformity is obtained by sieving the powder and is calculated as follows:

$$\frac{\text{Particle size of which 60\% of the powder passes}}{\text{Particle size of which 10\% of the powder passes}} = \text{Uniformity Index.}$$

As narrow as the particle size distribution is, the index becomes close to 1. This uniformity index is applied when the powder is rather coarse and not so cohesive. For the fine and cohesive powder, "Cohesion" degree is used.

After measuring various properties, the Table 1 is used for converting the measured figures into the index numbers. The total of these index numbers indicate the Flowability Index. The three columns in the left of the table will give an idea about the necessity for bridge breaching measures.

9-2 Floodability Evaluation:

For the numerical evaluation of the Floodability the following four properties are applied:

1. Flowability (This is obtained as the index with the method mentioned above. With the material possible to flush, the higher the flowability is, the higher is the degree of floodability.)
2. Angle of Fall.
3. Angle of Difference
4. Dispersibility.

With the Table 2 the measured properties are converted into the index numbers. The total of these index numbers are the Floodability Index. From the three columns on the left the powder's Floodability can be judged and also whether sealing is necessary or not.

Degree of Flowability	Flowability Index	Necessity of Bridge-breaking measures	Angle of Repose		Compressibility		Angle of Spatula		Uniformity*		Cohesion**	
			Degree	Index	%	Index	Degree	Index	No.	Index	%	Index
Very Good	90 – 100	Not required	<25 26 – 29 30	25 24 22.5	<5 6 – 9 10	25 23 22.5	<25 26 – 30 31	25 24 22.5	1 2 – 4 5	25 23 22.5		
Fairly Good	80 – 89	Not required	31 32 – 34 35	22 21 20	11 12 – 14 15	22 21 20	32 33 – 37 38	22 21 20	6 7 8	22 21 20		
Good	70 – 79	Sometimes Vibrator is required	36 37 – 39 40	19.5 18 17.5	16 17 – 19 20	19.5 18 17.5	39 40 – 44 45	19.5 18 17.5	9 10 – 11 12	19 18 17.5		
Normal	60 – 69	Bridging will take place at the marginal point	41 42 – 44 45	17 16 15	21 22 – 24 25	17 16 15	46 47 – 59 60	17 16 15	13 14 – 16 17	17 16 15	<6	15
Not Good	40 – 59	Required	46 47 – 54 55	14.5 12 10	26 27 – 30 31	14.5 12 10	61 62 – 74 75	14.5 12 10	18 19 – 21 22	14.5 12 10	6 – 9 10 – 29 30	14.5 12 10
Bad	20 – 39	Powerful measures should be provided	56 57 – 64 65	9.5 7 5	32 33 – 36 37	9.5 7 5	76 77 – 89 90	9.5 7 5	23 24 – 26 27	9.5 7 5	31 32 – 54 55	9.5 7 5
Very Bad	0 – 19	Special apparatus and techniques are required.	66 67 – 89 90	4.5 2 0	38 39 – 45 >45	4.5 2 0	91 92 – 99 >99	4.5 2 0	28 29 – 35 >35	4.5 2 0	56 57 – 79 >79	4.5 2 0

* Use these figure for granules or granular powder with which the uniformity can be measured.

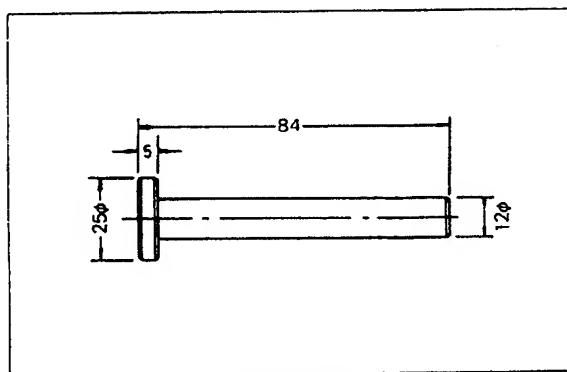
** Apply these figures for fine and cohesive powders with which the cohesion can be measured.

Degree of Floodability	Floodability Index	Measures for Flushing Prevention	Flowability		Angle of Fall		Angle of Difference		Dispersibility	
			Index from Table 1	Index	Degree	Index	Degree	Index	%	Index
Very high	80 - 100	Rotary seal must be used	>60	25	<10	25	>30	25	>50	25
			59 - 56	24	11 - 19	24	29 - 28	24	49 - 44	24
			55	22.5	20	22.5	27	22.5	43	22.5
			54	22	21	22	26	22	42	22
Fairly High	60 - 79	Rotary seal is required	53 - 50	21	22 - 24	21	25	21	41 - 36	21
			49	20	25	20	24	20	35	20
			48	19.5	26	19.5	23	19.5	34	19.5
			47 - 45	18	27 - 29	18	22 - 20	18	33 - 29	18
Tends to flush	40 - 59	Sometimes Rotary seal is required	44	17.5	30	17.5	19	17.5	28	17.5
			43	17	31	17	18	17	27	17
			42 - 40	16	32 - 39	16	17 - 16	16	26 - 21	16
			39	15	40	15	15	15	20	15
May flush	25 - 39	Rotary seal is necessary depending on flow speed and feeding conditions	38	14.5	41	14.5	14	14.5	19	14.5
			37 - 34	12	42 - 49	12	13 - 11	12	18 - 11	12
			33	10	50	10	10	10	10	10
			32	9.5	51	9.5	9	9.5	9	9.5
Won't flush	0 - 24	Not required	31 - 29	8	52 - 56	8	8	8	8	8
			28	6.25	57	6.25	7	6.25	7	6.25
			27	6	58	6	6	6	6	6
			26 - 23	3	59 - 64	3	5 - 1	3	5 - 1	3
			23	0	>64	0	0	0	0	0

Remarks: The above tables are reprinted from "Chemical Engineering" pages 166 and 167 of January 18, 1965, with approval of Mr. Ralph Carr, Jr., and the copyright owner, McGraw-Hill Incorporated, New York, N.Y., 10036, U.S.A.

10. MAINTENANCE

1. Occasionally, remove tapping pin and clean its sliding surface with a dry cloth. If the powder sticks to the pin, then the pin will be prevented from smooth operation. When the contacting surface of the cam wears out then it should be replaced with a new one. Tapping pin is made of abrasion resisting nylon.



Sketch 38

2. Pan holder for measuring angle of spatula can be removed by pulling it out of the main body. Occasionally clean the sliding surface of the pan holder.
3. For any problem or for need of replacement parts, please contact Distributor in your area or Hosokawa International Inc., No. 10, 2-Chome, Minami-Kyutaro Machi, Higashi-Ku, Osaka, 541, Japan.

Metal Oxide Surface Additives for Xerographic Toner: Adhesive Forces and Powder Flow

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Abstract

Xerographic toners use submicron metal oxide surface additives to control powder flow. Indeed, oxides have been used to improve flowability or compressibility of cohesive powders for decades, from coffee whitener to aspirin. To date there has been little attempt to understand the mechanism of action of flow aids. In this paper, toner powder cohesion was measured with respect to the primary particle size, hydrophobicity, and hydrogen bonding of the oxide. Cohesion is interpreted in terms Van der Waals, capillary, and hydrogen bonding forces. Flow with oxides is determined by the nano-geometry of contact between oxide particles, determined by the oxide primary particle size. Adhesion forces decrease with decreasing oxide primary particle size and increasing hydrophobicity.

Introduction

This paper studies adhesion of toner with surface oxides (used to control toner flow, charge¹⁻⁵ and transfer.⁶)

Experimental

Toner flow was measured on a Hosokawa Micron Powder tester, which applies a vibration for 90 s to 2 g of toner on a set of sieves (Figure 1). The % cohesion is:

$$\% \text{ cohesion} = 50 \bullet A + 30 \bullet B + 10 \bullet C \quad (1)$$

A, B and C are the toner weights left on each screen. Eq 1 applies a weighting factor proportional to screen size.

Table 1 lists the toners used; Table 2 the oxides. Additives were blended at 24 krpm using a coffee mill.

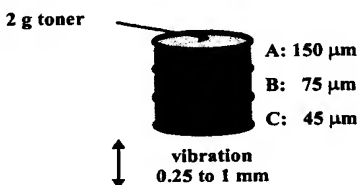


Figure 1. Powder cohesion test setup.

Table 1. Base Toner Particles

Toner ID	Resin ID	Pigment Type	wt%
A1-A3	1	unoxidized CB	6.0
B1-B5	2	cyan	4.0
C	3	none	0
D	3	oxidized carbon black	4.2
E	3	oxidized carbon black	7.2
F	3	unoxidized carbon black	4.7
G	3	unoxidized carbon black	19.3
H	3	magenta	6.0
I	3	cyan	6.0
J1,J2	4	cyan	6.0
K1,K2	5	none	0

Table 2. Flow Additives

Additive	Base Oxide	Treated	Hydrophobic	H-Bonds
Degussa A380	7 nm silica	none	no	yes
Degussa R812	7 nm silica	HMDS	yes	no
Degussa MOX170	15 nm silica	none	no	yes
Degussa R972	16 nm silica	DMCS	yes	no
Degussa TT600	40 nm silica	none	no	yes
Degussa P25	21 nm TiO ₂	none HMDS	no yes ^a	no no
Degussa Al ₂ O ₃	20 nm Al ₂ O ₃	none HMDS	no yes	no no
A*	100 nm *	*	no	no

* Proprietary; HMDS = ((CH₃)₂SiN)₂; DMCS = (CH₃)₃SiCl₂

Results and Discussion

Powder Cohesion Test and Interparticle Forces

The literature is silent except for Carr's assertion⁷ that there is a quantitative relationship between adhesive force and Hosokawa cohesion. Toner consists of agglomerated particles. Assume that the ensemble cohesion follows a Gaussian distribution (eq 2 and Figure 2).

$$N_F = \frac{N_0}{\sqrt{2\pi} \sigma} \exp \left(-\frac{(F - \bar{F})^2}{2\sigma^2} \right) \quad (2)$$

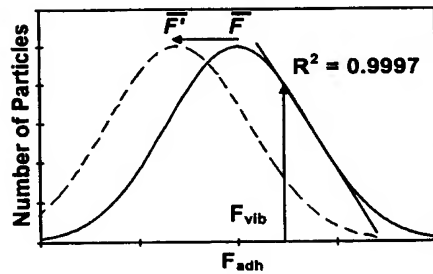


Figure 2. Relationship between Gaussian toner force distribution and Hosokawa powder cohesion test. Two powders of different average interparticle forces are shown.

The screen vibration applies a defined force, F_{vib} , to the toner. If F_{vib} is large enough to break the agglomerates they will go through the screen. If F_{vib} is large enough to separate $\approx 60\%$ of the particles (but less than $\approx 90\%$), as shown in Figure 2 (\bar{F} = average cohesive force), then the number of particles separated will be linearly related to F_{vib} . Similarly, if the average particle cohesive force changes from \bar{F} to \bar{F}' (Figure 2), at constant F_{vib} , then the number of particles that will pass through the screens is linear in \bar{F} . Carr⁷ has been clever in using different size screens. The smaller screen requires a larger force to pass toner. Even if all the toner passes one screen, the smaller screen below can partition toner in its linear range, extending the measurement range. There are two hidden assumptions. The first is that cohesion is linear in screen size. The second is that the width of the cohesive force distribution is constant. For example, narrowing the distribution results in an apparent lower cohesion for the conditions in Figure 2, even if \bar{F} is unchanged. This too is compensated by different size screens, at least if there is toner on more than one screen (a screen on each side of \bar{F} in Figure 2).

Overall, there is a reason to expect an approximately linear relation between Hosokawa cohesion and interparticle forces, provided that $\approx 10\%$ to 40% (or 60 to 90%) of toner is on at least one screen. This condition is fulfilled for tests here (excepting those below 2% cohesion).

Surface Coverage of Additives on Toner

Oxide surface coverage was estimated assuming a spherical oxide primary particle of radius r , and a spherical toner of radius, R . Eq 2 assumes the particles pack in hexagonal close packing. For 100% surface coverage:⁹

$$wt\% \text{ additive} = 100 \cdot \frac{2 \cdot \pi}{\sqrt{3}} \cdot \frac{\rho_a \cdot r}{\rho_t \cdot R} \quad (3)$$

In fact, oxides are fractal fused aggregates of primary spherical particles, which are not broken down during toner blending. Thus, while primary sizes are often quoted, the aggregate on the toner is larger: 300 to 500 nm. Due to the fractal architecture these particles will not cover all the toner surface expected, as shown in Figure 3.

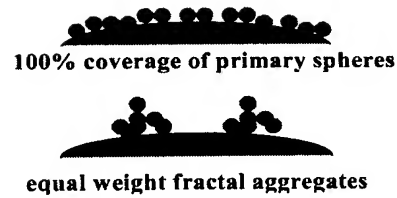


Figure 3. Additives on surface of toner after blending.

Van der Waals Forces

All materials are subject to Van der Waals forces, which depends on instantaneous polarization of electrons in one material due to electromagnetic interaction with electrons in another material, as derived by Lifshitz¹⁰:

$$F_v = \frac{\hbar \omega r}{16 \pi L^2} \quad (4)$$

$\hbar \omega$ (10^{11} to 10^{13} ergs) depends on the materials and intervening medium ($\epsilon_{\text{materials}}$, ϵ_{medium} , $n_{\text{materials}}$ and n_{medium} , where n = refractive index and ϵ = dielectric constant), \hbar is Planck's constant, L is the Van der Waals contact distance (≈ 0.5 nm), and r is the contact radius of the curvature from surface asperities. If there are surface additives then r is the radius of the oxide primaries (not the aggregate).

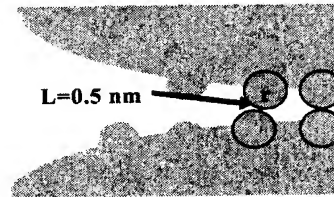


Figure 4. The contact of toner particles at asperities.

Capillary Forces

Water on surfaces creates capillary forces.¹¹⁻¹³ Water is in a pendular state on toner (Figure 5), as there are less than a few monolayers (0.35 nm/monolayer.¹³). The water is insufficient to bridge asperities (which are 50 to 100 nm for bare toner, or 7 to 50 nm with flow aid, as shown later). The water meniscus creates a force:¹¹⁻¹³

$$F_{\text{capillary}} = 2 \pi r \sigma_w (1 - L/2) \quad (5)$$

Here, σ_w is the tensile strength of water (9.8×10^7 dynes/cm²), and l = thickness of the water layer.

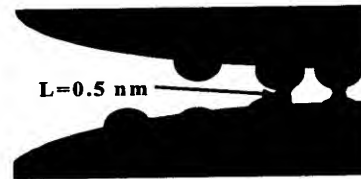


Figure 5. Pendular water between toner asperities.

Hydrogen Bonding

Toner surface groups that form hydrogen bonds will create an interparticle force. Figure 6 shows the contact of two silica primaries of radius r . Interparticle H-bonds form between -OH groups within an area, S_{H-bond} , of "radius" a from the "contact". Outside this area the water layer separation, $2L$ (=H-bond length), is too large for an H-bond, due to surface curvature. Since $a \ll r$, $S_{H-bond} = \pi a^2$, $s = r\theta \approx h \approx a$, $\sin \theta \approx \theta$, and $L = h \cdot \sin(\theta/2)$.

$$S_{H-bond} = \pi a^2 = \pi (r\theta) (L/\sin(\theta/2)) = 2\pi r L \quad (6)$$

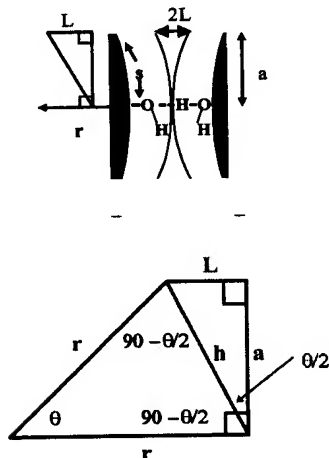


Figure 6. Geometry for interparticle H-bond area in eq 6.

The adhesive force is (ρ_{H-bond} = surface area density of H-bonds, and f_{H-bond} = bond strength):

$$F_{H-Bond} = 2 \pi L \rho_{H-Bond} f_{H-Bond} r \quad (7)$$

Overall, all of the interparticle forces are linear in the asperity radius: larger asperities result in larger forces.

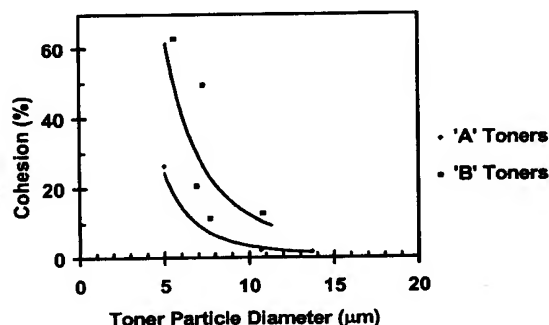


Figure 7. Powder cohesion with toner particle size.

Toner Powder Flow Cohesion Tests

Why do we now worry about flow when early toners had no flow additives? Figure 7 shows one reason, illustrated by two toner series. In each series decreased

particle size shows a dramatic cohesion increase. The current trend to small toner increases the need for flow additives.

Figure 8 shows that as the loading of pigment changes there is a linear change in cohesion. For small carbon blacks, less than 60 nm in primary size (black toners), cohesion drops linearly with pigment loading. The smaller the pigment, the larger the effect as a flow aid, as expected from eq 4, 5 and 7. To act in this way, pigment must be on the toner surface, proportional to the bulk concentration. Color pigments are larger than these carbon blacks, and show a linear increase in cohesion with loading. Thus, the bare toner asperity size is 60 to 100 nm: smaller pigments are flow aids, larger pigment particles are adhesives.

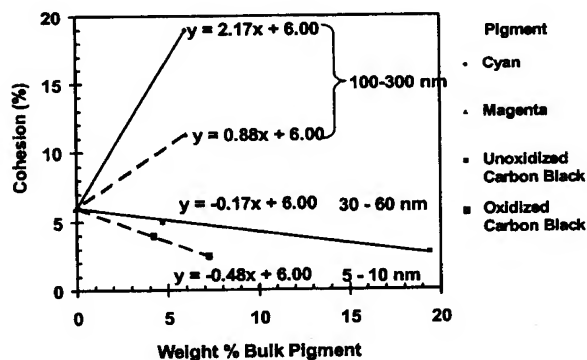


Figure 8. Toner cohesion with pigment type and loading.

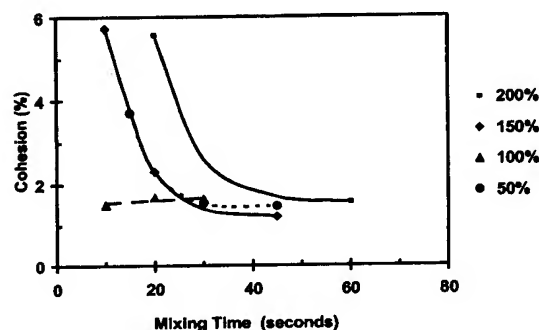


Figure 9. Coffee mill blending of R812 on toner J2

Figure 9 shows toner cohesion with additive blending time for various theoretical coverage's (eq 3). At 50% coverage cohesion drops rapidly, close to the lower limit of the cohesion test (1.5 %). At 100% coverage, cohesion remains low over all blend times studied, while above 100% coverage, cohesion again drops rapidly. This behaviour is reasonable. If there is barely enough additive, then good surface coverage requires perfect dispersion; if there is sufficient additive a poor dispersion is tolerable. Above the required loading, excess additive will be loose, not on the

toner surface. This impedes flow until the loose additive is blended in (R812 silica alone, without toner, has a cohesion of 60%!!).

Figure 10 shows the cohesion, measured at the optimal blend time, for each surface coverage (from Figure 9). This optimal cohesion is independent of coverage, from 50% to 250%. Only at 25% coverage is cohesion higher. Thus, while it takes longer to blend at 50% or 250% theoretical coverage, equivalent flow to 100% coverage is ultimately obtained. A second toner (blend optimization not shown) does show reduced cohesion between 50% and 100% coverage. While it is not clear why the toners behave differently, in both cases near 100% coverage, based on eq 3, does indeed give optimal flow.

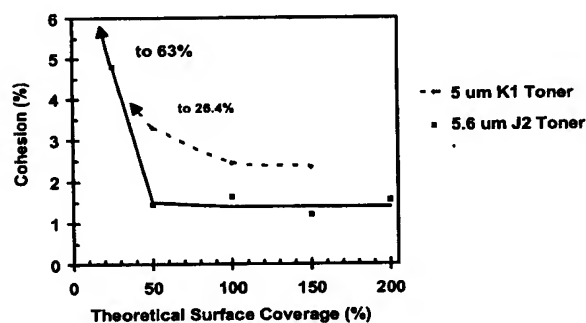


Figure 10. Optimal cohesion with additive coverage.

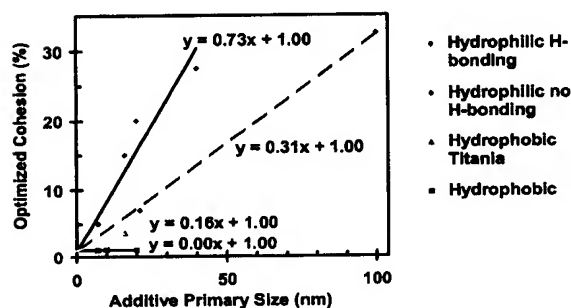


Figure 11. Cohesion with additive size and type (Toner J2)

Figure 11 shows the optimal cohesion (blending data not shown) at 100% oxide coverage, grouped according to oxide properties. Hydrophilic additives capable of H-bonding (untreated oxides with surface OH groups that form strong H-bonds) have the largest interparticle forces, due to the H-bond, Van der Waals and capillary forces. Cohesion increases linearly with the additive primary radius, as expected from eq's 4, 5 and 7. Lower cohesion arises with hydrophilic additives that do not form strong H-bonds. These additives also show the expected linear increase in

cohesion with additive primary size (eq 4 and 5), but with reduced size dependence (by a factor of 2.5) due to the lack of H-bonds. The lowest cohesion is obtained with hydrophobic oxides. These are silicas treated to render them hydrophobic, removing any OH groups that might form H-bonds. The cohesion with these additives is so good that the lower test limit is exceeded. To extend the test, less vibration amplitude is needed.

Figure 12 shows the effect of reduced vibration on hydrophobic additives. As the vibration decreases from the standard 1 mm vibration, cohesion increases rapidly. Figure 12 shows that cohesion does increase linearly with additive size, as expected for Van der Waals' forces (eq 3).

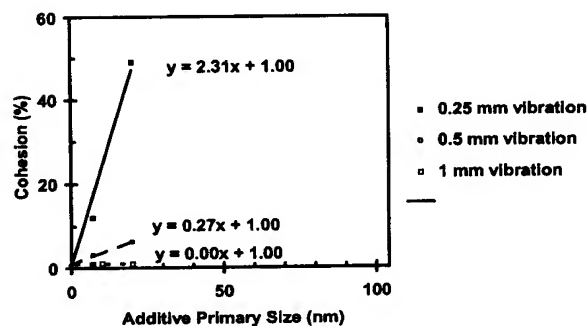


Figure 12. Cohesion with hydrophobic additives.

Conclusions

Toner flow with surface additives depends on Van der Waals, capillary, and hydrogen bonding forces, and is determined by the nano-geometry of contact. Cohesion decreases with increasing hydrophobicity, decreasing hydrogen bonding, and decreasing size.

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Biography

Dr. Veregin has an M.Sc. and Ph.D. in Chemistry, joining the Xerox Research Centre of Canada 13 years ago. His interests include xerographic physics, surfaces, ESR, and polymerization kinetics. He has authored 48 papers, is an inventor on 29 US patents, and is a recipient of the A. K. Doolittle Award from the American Chemical Society.

APPENDIX C - RELATED PROCEEDINGS APPENDIX

NONE